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THE PHOTOLYSIS OF ACETONE ABOVE 300° C.[1]

BY L. MANDELCORN[2] AND E. W. R. STEACIE

ABSTRACT

Acetone has been photolyzed at temperatures above 300° C. The formation of ethylene becomes of increasing importance at higher temperatures. The normal kinetics of the reaction are followed, however, and ethylene does not appear to be formed at the expense of ethane or methane.

INTRODUCTION

The production of methane and ethane in the acetone photolysis at temperatures below 300° C. is well accounted for by the reactions (3, 4)

$$2CH_3 \rightarrow C_2H_6 \qquad [2]$$

$$CH_3 + CH_3COCH_3 \rightarrow CH_4 + CH_3COCH_2. \qquad [3]$$

On this basis

$$\frac{k_3}{k_2^{\frac{1}{2}}} = \frac{R_{CH_4}}{R_{C_2H_6}^{\frac{1}{2}} [CH_3COCH_3]} .$$

It has, however, been found that ethylene becomes a product at higher temperatures (1, 5). It appeared to be desirable to determine if the formation of ethylene at higher temperatures complicated the kinetics of the photolysis.

EXPERIMENTAL

The apparatus and procedure were the same as in a previous investigation (2), with the reaction cell isolated by a mercury cutoff (reaction volume = 195 cc.). To get sufficient amounts of ethane the full intensity of a Hanovia S-100 lamp was used. Methane and carbon monoxide were separated from a trap cooled with solid nitrogen to ensure that ethylene was retained. Ethane and ethylene were determined by mass spectrometric analysis of the C_2 fraction.

RESULTS

The results are given in Table I. They include two experiments at reduced light intensity, and one experiment in which water vapor was added in an

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[2] *National Research Council of Canada Postdoctorate Fellow 1951–53.*

TABLE I

PRODUCTS OF PHOTOLYSIS OF ACETONE

Temp., °C.	Time, sec.	$[CH_3COCH_3] \times 10^6$ M./cc.	R_{CH_4}	$R_{C_2H_6}$	$R_{C_2H_4}$	R_{CO}	$\frac{k_3}{k_2^{\frac{1}{2}}} \times 10^{13} \left\{\frac{\text{cc.}}{\text{molecules-sec.}}\right\}^{\frac{1}{2}}$
			$\times 10^5$ cc. N.T.P./sec.				
284*	3600	1.77	8.47	0.44	0.05	6.15	136
318	1500	1.73	33.9	2.30	0.41	26.1	250
332	1500	1.77	37.7	1.72	0.50	28.1	313
344	1800	1.76	35.2	1.29	0.52	25.4	338
352	1200	1.75	42.1	1.46	0.64	29.1	387
375	1380	1.78	49.5	1.17	1.00	30.9	500
408	1200	1.74	59.8	0.88	2.12	38.7	705
434	1500	1.75	66.1	0.88	3.41	41.9	850
439	900	1.75	73.3	0.82	4.88	41.5	890
271	1800	0.86	10.3	3.20	0.11	11.2	129
291	1800	0.91	13.2	2.44	0.16	12.7	181
309	1800	0.83	13.8	1.76	0.16	12.2	242
325	1500	0.86	16.7	1.48	0.22	13.8	310
341	1500	0.94	20.9	1.33	0.27	16.2	374
342**	7800	0.86	5.81	0.14	0.09	4.09	358
343	1800	0.86***	17.5	1.03	0.30	13.3	388
362	1500	0.91	23.4	0.97	0.48	17.2	512
374	1200	0.89	26.5	1.00	0.48	18.9	575
392	1200	0.87	27.7	0.77	0.77	18.9	708

* *Corning No. 9863 filter.*
** *Two No. 9863 filters.*
*** *Plus* $[H_2O] = 0.38 \times 10^{-6}$ *M./cc.*

attempt to detect ketene by the formation of acetic acid. The test was negative.

An Arrhenius plot of the results is given in Fig. 1. The equation of the line is

$$13 + \log \frac{k_3}{k_2^{\frac{1}{2}}} = 6.03 - \frac{2.13 \times 10^3}{T},$$

corresponding to $E_3 - \frac{1}{2}E_2 = 9.8$ kcal., $P_3/P_2^{\frac{1}{2}} = 25 \times 10^{-4}$ (at 350° C.). These values are in good agreement with previous work, including the tendency for the ratio $k_3/k_2^{\frac{1}{2}}$ to increase somewhat with decreasing acetone concentration. It is evident, therefore, that the formation of ethylene is independent of the mechanism of formation of ethane and methane. The reaction follows the normal kinetics in spite of the considerable formation of ethylene. The source of the ethylene is uncertain. In the photolysis of diethyl ketone ethylene is formed at high temperatures by the decomposition of the pentanonyl radical

$$C_2H_4COC_2H_5 \rightarrow C_2H_4 + CO + C_2H_5.$$

It is possible that ethylene in the present case arises from hydrogen abstraction from methyl ethyl ketone, followed by the breakup of the resulting radical

$$CH_3COC_2H_4 \rightarrow CH_3 + CO + C_2H_4.$$

This would give the reaction chain characteristics, but the total amount of ethylene formed is quite small, and the effect on the quantum yield of CO formation would be very slight.

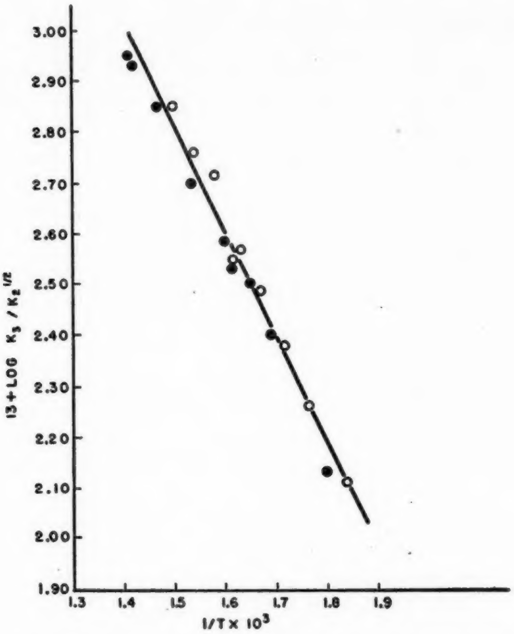

FIG. 1. Arrhenius plot for the abstraction of hydrogen from acetone by methyl radicals.
Filled circles—acetone conc. = 1.76×10^{-6} M./cc.
Open circles—acetone conc. = 0.88×10^{-6} M./cc.

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PREPARATION OF 1-C^{14} PENTONIC ACIDS BY THE CYANHYDRIN SYNTHESIS[1]

By A. C. Neish

ABSTRACT

Solutions of pure D-threose and D-erythrose, buffered with bicarbonate (0.82 moles) plus carbonate (0.18 moles), were treated with an equimolar amount of C^{14}-labeled KCN. The aldonic acids were isolated as salts, using carrier technique, in yields of 90–95% based on the radioactive carbon. D-Erythrose gave 1.89 times as much arabonic as ribonic acid while D-threose gave 2.36 times as much lyxonic as xylonic acid. Despite the unfavorable ratio in the latter case it was found that D-xylose could be obtained in an over-all yield of 22%, based on the cyanide.

Interest in the metabolism of pentoses by bacteria has prompted an investigation on the cyanhydrin synthesis as a method for preparing 1-C^{14}-labeled pentoses. L-Arabinose-1-C^{14} has been made, in yields of about 3% (12), by the nitromethane synthesis while D-xylose-1-C^{14} (13) has been prepared from glucose-1-C^{14}. As far as the present writer knows pentonic acids have never been prepared by the cyanhydrin reaction, so there is no information on the yields of isomers to be expected. The ratio of epimers would be expected to vary with the pH of the cyanide reaction mixture (10) and a complete investigation should include a study of this important factor. The present paper gives information on the yields of pentonic acids obtained from D-erythrose and D-threose under one set of conditions. Since the results indicate that the cyanhydrin reaction is a convenient route for preparing C^{14}-labeled pentoses this information may be of value to other workers.

Deionized solutions of threose or erythrose, prepared by the Ruff degradation, contained at least one other reducing substance so they were not used. D-Erythrose was obtained from 4,6-ethylidene-D-glucitol (9), the intermediate 2,4-ethylidene-D-erythrose being purified by distillation. D-Threose was prepared from 1,3-benzylidene-D-arabitol. The intermediate 2,4-benzylidene-D-threose crystallized, unexpectedly, so it was not necessary to convert it to the isopropylidene derivative for purification. The solutions of tetroses obtained by these methods were pure as far as could be ascertained by paper chromatography.

The cyanhydrin reaction and hydrolysis of the amides was done following the work of Isbell *et al.* (10) on preparation of D-glucose-1-C^{14}. The aldonic acids were separated using methods developed for epimerization studies (3, 4). Since high specific activities were not required, these separations were simplified by the use of carriers. The yields were good, 90–95% of the C^{14} being recovered as aldonic acids. D-Erythrose gave arabonic and ribonic acids in the ratio of 1.89: 1 while D-threose gave lyxonic and xylonic acids in the ratio of 2.36: 1 respectively.

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The conversion of these acids to the aldoses has not been thoroughly investigated. It has been pointed out by Isbell *et al.* (10) that there is no universal procedure for the sodium amalgam reduction of lactones which will give maximum yields with all lactones. They found that glucono-δ-lactone gave excellent yields in an oxalate buffered medium while mannonic-γ-lactone gave better yields in a benzoate buffered medium and required more amalgam. We have investigated the reduction of xylono lactone and obtained better yields in an oxalate buffered medium than in a benzoate buffered one but it required twice as much amalgam as glucono-δ-lactone. The yield of xylose was about 80%, based on the cadmium D-xylonate cadmium bromide double salt. Presumably the other aldonic acids could be converted to pentoses in similar yields under the best conditions. D-Arabinose-1-C^{14} could then be used for preparation of D-glucose-2-C^{14} in good yields, by addition of inactive cyanide (10). In both of the cyanhydrin reactions, starting with D-erythrose, the epimer needed for this synthesis is formed in the highest yield.

EXPERIMENTAL

Methods

Unless stated otherwise evaporations were carried out in a Craig evaporator (2) using a bath temperature of 40–45° C. and the full vacuum of a filter pump (20–25 mm.). The aldose content of the solutions was determined by hypoiodite oxidation (8). Measurements of radioactivity were made using a windowless counter operating in the proportional region. The samples were plated on aluminum disks and were so small that self absorption was negligible. The counting assembly was calibrated against the U.S. National Bureau of Standards carbon-14 standard; a sodium carbonate solution rated at 1280 disintegrations per second/ml. The results were expressed as millicuries. Paper chromatography of the tetrose solutions was carried out with Whatman No. 1 paper using the descending technique. Methyl ethyl ketone saturated with water was the only developing solvent used. Spots of reducing substances were detected by three spray reagents; molybdate (1), alkaline dinitrosalicylate (11) and triphenyl-tetrazolium chloride (15). The tetrazolium spray is much more sensitive for tetroses than glucose, whereas the other sprays are about equally sensitive for glucose and the tetroses.

Preparation of Tetroses by the Ruff Degradation

Ruff degradation (5) of Ca-D-arabonate and Sr-D-xylonate gave solutions of D-erythrose and D-threose. Analysis of the deionized solutions for aldose indicated yields of 36% and 40% of the theoretical, respectively. However, paper chromatography showed at least two reducing substances to be present in each solution, both being detected by all three sprays as spots of about equal intensity. One component migrated at the same rate as the tetroses, and the other at about half the rate. A pure tetrose fraction could probably be obtained by chromatographic fractionation of these solutions. However the tetrose solutions used in the cyanhydrin reactions were prepared by other methods, described below, which gave chromatographically pure solutions directly.

2,4-Ethylidene-D-Erythrose

4,6-Ethylidene-D-glucitol (10.4 gm., 50 mM.) (9) was dissolved in 150 ml. of ice-cold water and treated with an ice-cold solution containing 23.94 gm. (105 mM.) of H_5IO_6 in 150 ml. of water. After 10 min. the mixture was neutralized to the phenolphthalein end point by a warm concentrated solution of strontium hydroxide. The precipitate was filtered out and the filtrate evaporated to dryness. The residue was extracted with alcohol, the alcohol evaporated, and the sirup distilled through a short column, under reduced pressure, to give 1.5 gm. of 2,4-ethylidene-D-erythrose, b.p. 98° C. at 8 mm., as the only fraction. This material was a colorless glass; $[\alpha]_D^{22}$ $-41.36°$ (*c*, 2.5, water). It gave 91.2% of the expected amount of acetaldehyde on hydrolysis by 0.5 *N* sulphuric acid, followed by distillation, as measured by the bisulphite binding capacity of the distillate. This rotation is a somewhat higher than the value $[\alpha]_D$ 36, reported for the L-isomer (12).

D-Erythrose

A solution of 1.08 gm. (7.4 mM.) of 2,4-ethylidene-D-erythrose was dissolved in 45 ml. of water and 6–8 ml. of IR-120-H Amberlite cation-exchange resin added. This mixture was distilled at constant volume for 1.5 hr. to effect hydrolysis and removal of the acetaldehyde. The residue was treated with charcoal and filtered. The colorless solution thus obtained was found to contain 5.71 mM. of aldose. A portion was chromatographed on paper as described above and found to give only one spot with an R_f of 0.21 (glucose had R_f of 0.055 on same sheet). An aliquot of this solution was used for the cyanhydrin synthesis described below.

Reaction of C^{14}-labeled Cyanide with D-Erythrose

A solution containing 2 mM. of $KC^{14}N$ (1 millicurie) and 0.36 mM. of KOH in 10 ml. of water was frozen solid in a 50 ml. glass stoppered Erlenmeyer flask immersed in a dry ice bath. An aliquot of the D-erythrose solution (14.1 ml., 2 mM.) containing 2 mM. of $NaHCO_3$ was added, the stoppered flask allowed to stand two days at room temperature, and then 1.64 ml. of *N* NaOH added. After two more days at room temperature the mixture was heated to 60° C. and aerated to remove the ammonia released by hydrolysis of the amides. This ammonia was caught in standard acid and measured by back titration. A total of 1.85 m.e. (92.5%) was recovered in five hours, at which time the volume had decreased to about one-third and the hydrolysis was complete. The residue was transferred to a beaker containing 25 ml. of IR-120-H Amberlite cation-exchange resin, stirred, and then transferred to a column containing an additional 25 ml. of the resin. The effluent was treated with 2 gm. of Ca-D-arabonate carrier and the mixture warmed with 0.3 gm. of calcium carbonate, filtered, and the filtrate concentrated to about 8 ml. and crystallization induced by addition of methanol. The Ca-D-arabonate which separated (2.3 gm., 0.635 mc.) was recrystallized from methanol–water to constant specific activity to give 2.25 gm. (0.590 mc.). The mother liquors were combined, concentrated to remove methanol, diluted with water, passed through an IR-120-H column to remove the calcium ions, boiled with 0.4 gm.

of cadmium carbonate in the presence of 2 gm. of Cd-D-ribonate carrier, filtered, and the filtrate concentrated and crystallized from methanol–water. After recrystallizing to constant specific activity, 1.97 gm. (0.312 mc.) of Cd-D-ribonate was obtained. Thus the ratio of arabonate: ribonate was 1.89, and a total of 90.2% of the C^{14} added as cyanide was found in the aldonic acids.

2,4-Benzylidene-D-Threose

A solution of 5 gm. of 1,3-benzylidene-D-arabitol (7) in 150 ml. of warm water was cooled to 30° C. and mixed with 50 ml. of 9.45% $NaIO_4$. After one hour at room temperature, 14.5 ml. of molar barium acetate was added. The mixture was filtered and the filtrate concentrated in a flask containing 1 gm. of $BaCO_3$. The residue was dehydrated by three successive evaporations with 25 ml. portions of absolute ethanol, then dissolved in ethanol and filtered. The filtrate was concentrated to a sirup and allowed to stand one hour at room temperature. This was treated with 100 ml. of water, and a crystalline residue formed, which was filtered out and washed with water giving 2.4 gm. melting at 160–161° C. This melting point was raised to 165.5° C. by recrystallization from ethanol. Found: $[\alpha]_D^{22}$ 77.6° (*c*, 2, pyridine), C, 63.32; H, 5.82. Calculated for $C_{11}H_{12}O_4$: C, 63.45, H, 5.81. This compound was obtained only as a sirup by previous workers (14), who carried out this oxidation using lead tetraacetate. However, a crystalline benzylidene-L-threose hemihydrate, m.p. 119–120° C., has been reported (6).

D-Threose

A solution of 1.7 gm. of 2,4-benzylidene-D-threose in 40 ml. of 10% acetic acid was refluxed for one hour, concentrated to a sirup, and the residue, after addition of 20 ml. of water, was extracted three times with ether to remove the last traces of benzaldehyde. The aqueous phase was again evaporated to a sirup and dissolved in 20 ml. of water to give a clear colorless solution, pH 5.0, containing 7.22 millimoles (88%) of aldose. Paper chromatography as described above showed the presence of only one reducing substance with an R_f of 0.22 (glucose had R_f of 0.055 on the same sheet). A portion of this solution was used in the cyanhydrin synthesis described below.

Reaction of C^{14}-labeled Cyanide with D-Threose

This reaction was carried out with 2 mM. (1 mc.) of cyanide as described for D-erythrose. The yield of ammonia on hydrolysis was 1.8 m.e. (90%). The solution of aldonic acids obtained, after removal of the cations, was warmed with 2 mM. of cadmium hydroxide and 5 mM. of cadmium carbonate, then treated with 10 m.e. of aqueous HBr and filtered. Inactive cadmium-D-xylonate cadmium bromide double salt (2 gm.) was dissolved in the filtrate, which was then concentrated until crystallization started. After this was allowed to stand overnight at 3° C., 1.98 gm. of the double salt was obtained. Recrystallization to constant specific activity from water, and reworking of the mother liquors, gave a total of 2.17 gm. (0.273 mc.) of cadmium xylonate cadmium bromide. Addition of more carrier to the combined mother liquors, followed by reisolation, gave only 0.011 mc. more. Thus a total of 28.4% of the C^{14} was present as D-xylonic acid.

The combined mother liquors from the double salt were passed through an IR-120-H column containing 50 ml. of resin. The effluent was stirred one hour with 4 gm. of silver carbonate, filtered, and the bromide-free filtrate treated with 2 gm. of D-lyxono lactone and passed through a 25 ml. column of IR-120-H resin, to remove the silver ions. The effluent was concentrated to a sirup which was dehydrated by three evaporations with glacial acetic acid, giving finally 3 gm. of sirup. This was dissolved in 2 ml. of glacial acetic acid and cooled. Crystallization of the lactone was rapid. The product was recrystallized twice from acetic acid – ethyl acetate (about equal proportions) to give 1.73 gm. (0.260 mc.) of D-lyxono lactone. The mother liquors still contained a considerable amount of C^{14}, possibly because equilibrium had not been reached between the carrier lactone and the active lyxonic acid. In order to confirm this supposition another 2 gm. of inactive D-lyxono lactone was added to the mother liquors, the acetic acid removed by evaporation with water, and the aqueous solution titrated with N KOH to the phenol red end point until all the lactone was converted to the K salt. The potassium ions were then removed by an IR-120-H column and the effluent concentrated to a sirup and crystallized from glacial acetic acid as before. This time the crystallization required four days. After purification to constant specific activity 1.1 gm. (0.210 mc.) of D-lyxono lactone was obtained. The residue from this was rather gummy so another gram of carrier was added and reisolated by rapid crystallization giving another 1.1 gm. (0.100 mc.) of pure D-lyxono lactone. A total of 0.570 mc. of pure lactone was isolated and it was calculated, from the amounts of carrier added and recovered, that another 0.1 mc. was present in the residue. From these data about 67% of the C^{14} added as cyanide was converted to D-lyxonic acid. The ratio of lyxonic: xylonic acids was thus 2.36 and about 95% of the cyanide was converted to aldonic acids.

D-*Xylose-1-*C^{14}

Cadmium D-xylonate cadmium bromide (2.17 gm., 0.273 mc.) was dissolved in 125 ml. of warm water and the solution passed through a 50 ml. column of IR-120-H resin. The effluent was treated with 3.5 gm. of silver carbonate, filtered, and the bromide-free filtrate passed through a 35 ml. column of IR-120-H resin to remove silver ions. The effluent was evaporated to a sirup which was heated in a drying pistol, containing phosphorus pentoxide, at 100° C. (2 mm.) for 24 hr. to effect lactonization. The mixture of sirup and crystals thus obtained was dissolved in 120 ml. of water containing 4.2 gm. of oxalic acid dihydrate and 4.8 gm. of sodium oxalate. The mixture was stirred vigorously and 14 gm. of 5% sodium amalgam added. The temperature was maintained at 5–10° C. (ice-alcohol bath) and powdered oxalic acid added from time to time to keep the pH from rising above 4. After 30 min. another 14 gm. portion of the amalgam was added. When this was used up (about 45 min.) the mixture was filtered to remove mercury and excess sodium acid oxalate, the filter cake being washed with ice water. The filtrate was concentrated to about 50 ml., treated with 100 ml. of methanol, filtered again, diluted with an equal volume of water and neutralized by N NaOH, to the

phenol red end point, to convert any residual lactone to the sodium salt. Ordinary D-xylose (3 gm.) was dissolved in the solution which was then deionized by 50 ml. columns of IR-120 and IR-4B Amberlite resins in the acid and base forms, respectively. The deionized solution was concentrated to a sirup which was dehydrated by three evaporations with absolute ethanol and then crystallized from ethanol containing a little isopropanol. The first crop of crystalline D-xylose was 3.17 gm. (0.194 mc.). It was recrystallized by solution in 1 ml. of hot water followed by addition of 2 ml. of methanol and 4 ml. of ethanol. This gave 2.97 gm. with unchanged specific activity. A further 4 gm. of carrier was added to the mother liquors and another 3.52 gm. (0.027 mc.) of pure D-xylose isolated. The pure xylose isolated contained about 77% of the activity present in the cadmium double salt, another 3–4% remaining in the mother liquors.

Some glyoxylic acid, isolated as the 2,4-dinitrophenyl-hydrazone, was formed from the oxalate during reduction by sodium amalgam. It was necessary to remove this aldehyde-acid by deionization of the solution before the yield of aldose could be determined by the hypoiodite method. Experiments on the reduction of a sample of crystalline D-xylono lactone using acetic acid or benzoic acid as buffers gave only 35–40% yields of aldose. These yields were not increased by addition of an extra portion of sodium amalgam.

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A CHEMICAL SYNTHESIS OF D-TREHALOSE[1]

By R. U. Lemieux and H. F. Bauer

ABSTRACT

Chromatographic separation of the products formed on heating a mixture of the anomers of 2,3,4,6-tetra-*O*-acetyl-D-glucose and tri-*O*-acetyl-D-glucosan ⟨1,5⟩ α ⟨1,2⟩ at 100° C. afforded D-trehalose and the *neo*-D-trehalose of Haworth and Hickinbottom. Evidence was obtained to show that the latter compound is in fact α-D-glucopyranosyl β-D-glucopyranoside.

Three diastereoisomeric D-glucopyranosyl D-glucopyranosides are theoretically possible. The α,α-, β,β-, and α,β-forms have been termed trehalose (7), *iso*-trehalose (3, 7), and *neo*-trehalose (6), respectively. D-Trehalose occurs naturally in many lower plants and trehala (5). The substance has not previously been synthesized by chemical means. Leloir and Cahib (8) have recently reported an enzymic synthesis. *iso*-D-Trehalose (12) was first obtained by Fischer and Delbrück (3) as a by-product in the preparation of 2,3,4,6-tetra-*O*-acetyl-D-glucose. The identity of *neo*-D-trehalose is obscure. Vogel and Debowska-Kurnicka (19) obtained a substance, m.p. 68–70°, $[\alpha]_D$ +68.1 (chloroform), by condensing 2,3,4,6-tetra-*O*-acetyl-D-glucose in the presence of zinc chloride and phosphorus pentoxide. The product was assumed to be *neo*-D-trehalose octaacetate since the rotation was that expected on the basis of Hudson's rules of isorotation (7). Haworth and Hickinbottom (6) reacted 2,3,4,6-tetra-*O*-acetyl-β-D-glucose in benzene solution with Brigl's anhydride (2) to form the heptaacetate of a disaccharide termed *neo*-trehalose. The octaacetate melted at 140–141° C. with specific rotation +82° (chloroform). Sharp and Stacey (18) have recently questioned the identity of this substance and have reported the preparation of *neo*-D-trehalose octaacetate, m.p. 120°, specific rotation, +67° (chloroform), both by reaction of β-acetofluoroglucose with silver carbonate, "anhydrone", and iodine in chloroform and by treating 2,3,4,6-tetra-*O*-acetyl-α-D-glucose with phosphorus pentoxide in chloroform. More recently, Micheel and Hagel (14) reacted acetobromoglucose in acetone with about 0.4 moles of water in the presence of mercuric cyanide to form *iso*-trehalose octaacetate and a *neo*-trehalose octaacetate, m.p. 140°, $[\alpha]_D$ +80° (chloroform). These constants are in close agreement with those reported by Haworth and Hickinbottom (6). Since the present work was completed, a paper has appeared wherein Bredereck, Höschele, and Ruck (1) report melting 2,3,4,6-tetra-*O*-acetyl-β-D-glucose with zinc chloride to form *iso*-trehalose octaacetate and a *neo*-trehalose octaacetate, m.p. 140° C., $[\alpha]_D$ +64.4° (chloroform). We have reinvestigated the reaction of Brigl's anhydride with the anomeric 2,3,4,6-tetra-*O*-acetyl-D-glucoses.

A mixture of the anomeric 2,3,4,6-tetra-*O*-acetyl-D-glucoses (about 65% α-anomer) was heated in a small amount of benzene with an equimolar amount

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of tri-*O*-acetyl-D-glucosan ⟨1,5⟩ α ⟨1,2⟩ (Brigl's anhydride) (2) for 36 hr. at 100° C. The product was deacetylated and the disaccharides were isolated by preparative paper chromatography (15). This fraction was acetylated and the resulting mixture of sugar acetates was subjected to chromatographic separation on a column of Magnesol-Celite (5: 1) according to the general procedure of McNeely, Binkley, and Wolfrom (13). Two crystalline substances were isolated. One of the materials was identified as D-trehalose octaacetate. The other substance possessed the melting point and rotation reported by Haworth and Hickinbottom (6) for *neo*-D-trehalose octaacetate. Deacetylation of these substances afforded D-trehalose and a substance with the physical constants reported by Haworth and Hickinbottom for *neo*-trehalose (6).

Lemieux (9) has reviewed the previous experience in the preparation of α-D-glucopyranosides by reaction of alcohols with Brigl's anhydride and prepared β-D-maltose octaacetate by heating 1,2,3,6-tetra-*O*-acetyl-β-D-glucose with the anhydride and acetylating the product. Lemieux and Huber (11) have synthesized sucrose by reaction of the anhydride with 1,3,4,6-tetra-*O*-acetyl-D-fructose and deacetylation of the product. These syntheses as well as the synthesis of D-trehalose reported herein show that Brigl's anhydride has a strong tendency to form α-D-glucopyranosides when reacted with the secondary alcoholic or hemiacetal hydroxyl groups of partially acetylated sugars. Therefore, it is to be expected that Haworth and Hickinbottom (6) did in fact prepare an α-D-glucopyranoside on reacting Brigl's anhydride with 2,3,4,6-tetra-*O*-acetyl-β-D-glucose. There can be little doubt that the substance we have isolated is identical with the *neo*-D-trehalose reported by Haworth and Hickinbottom (6). A sample was hydrolyzed and paper chromatography showed the hydrolyzate to contain only glucose. Therefore, the nonreducing substance must be a D-glucosyl-D-glucoside. Periodate oxidation of the trehalose-type molecule should liberate two moles of formic acid and no formaldehyde. The new technique developed by Perlin (16) to measure the amount of formic acid liberated in periodate oxidations was used to study the periodate oxidation both of trehalose and of the *neo*-trehalose of Haworth and Hickinbottom. In each case, two moles of formic acid were liberated per mole of disaccharide and no appreciable amount of formaldehyde was formed. Therefore, the *neo*-trehalose of Haworth and Hickinbottom must be a D-glucopyranosyl D-glucopyranoside. The rotation in chloroform of the octaacetate, +82°, when compared (7) to those of D-trehalose octaacetate, +163°, and *iso*-D-trehalose octaacetate, −18.4° (12), leaves no doubt that the substance is in fact α-D-glucopyranosyl β-D-glucopyranoside.

EXPERIMENTAL

Octaacetates of D-*Trehalose and neo*-D-*Trehalose*

A solution of 2,3,4,6-tetra-*O*-acetyl-β-D-glucose (4), 4 gm., in 50 ml. of 96% ethanol was kept at 50° C. for 40 hr. The solution was concentrated *in vacuo* to a dry sirup which was dissolved in 50 ml. of dry ether. Skellysolve F was added to a slight turbidity and after seeding with starting material the solution was kept overnight at 0° C. The crystals which separated were removed by

filtration and the filtrate was evaporated *in vacuo* to a sirup $[\alpha]_D^{22}$ $+93°$ (chloroform). The substance (about 65% α-anomer), 2.15 gm., was dissolved in 25 ml. dry benzene. The solution was concentrated by distillation at atmospheric pressure to about 5 ml. volume and transferred to a tube which contained 1.90 gm. of Brigl's anhydride (2). The tube was sealed and heated at 100° C. for 36 hr. in a temperature-controlled oil bath. The product was deacetylated in methanolic ammonia and a 20% aqueous solution of the free sugars was applied as uniform streaks to 50×50 cm. sheets of Schleicher-Schuell No. 470A filter paper for chromatographic separation. About one milliliter of the solution was applied to each sheet. The sheets were attached to strips of Whatman No. 1 filter paper for downward irrigation (15) with butanol–pyridine–water (6: 4: 3). The band in the resulting chromatogram which was expected to contain disaccharides was readily detected on strips cut from the sheets by the periodate–permanganate spray reagent (10). After isolation by extraction with water and solvent removal, the disaccharides were acetylated with acetic anhydride and sodium acetate in the usual manner. The sirupy sugar acetates were dissolved in about 5 ml. of benzene and added to the top of a 160×35 mm. (in diam.) column of Magnesol-Celite (5: 1) (12) wetted with benzene. The chromatogram was developed with 1.5 liter of 60: 1 benzene – tertiary butanol mixture, the column was extruded and a streak was applied to the length of the column by spraying a freshly prepared aqueous solution of 1% potassium permanganate in 2.5 N aqueous sodium hydroxide through a 2 mm.-wide slit cut from a sheet of plexiglass. A diffuse zone extended from 8 to 60 mm. from the top of the column and a sharp zone from 65 to 90 mm. from the top of the column. Elution of the top zone with acetone gave 10 mgm. of a substance, m.p. 141–142° C., $[\alpha]_D^{25}$ $+ 81.8°$ (c, 0.4 in chloroform), after two crystallizations from ethanol. Haworth and Hickinbottom (6) have reported *neo*-D-trehalose octaacetate to melt at 140–141° C. with $[\alpha]_D$ $+82°$ (c, 5 in chloroform). The bottom zone was eluted with acetone to yield, after two crystallizations from ethanol, 15 mgm. of a substance, m.p. 100–101° C., $[\alpha]_D^{25}$ $+163°$ (c, 0.1 in chloroform). The melting point was undepressed by authentic D-trehalose octaacetate, m.p. 100–101° C. The infrared spectrum of the synthetic substance pressed with potassium bromide (17) into a window and measured with a Perkin–Elmer Model 21 spectrometer was identical to the spectrum of the authentic sample of D-trehalose octaacetate obtained under the same conditions.

D-*Trehalose*

The synthetic D-trehalose octaacetate was deacetylated in methanolic ammonia and the product was recrystallized from aqueous ethanol. The melting point of the substance, m.p. 97–98° C., was unaffected by mixture with an authentic sample of D-trehalose dihydrate of the same melting point.

neo-D-*Trehalose*

The synthetic *neo*-D-trehalose octaacetate was deacetylated with methanolic ammonia. The product obtained on crystallization from 90% ethanol sintered at 141–145° C. and melted in the range 195–210° C. All attempts to obtain a

sharply melting product were unsuccessful. Haworth and Hickinbottom (6) had the same difficulty and reported *neo*-trehalose to melt at 210–220° C. with sintering at 145–150° C. A sample was hydrolyzed in *N* hydrochloric acid. Paper partition chromatography using butanol–ethanol–water (5: 1: 4) and butanol–pyridine–water (6: 4: 3) detected only glucose in the hydrolyzate.

Periodate Oxidations

The disaccharides, 0.004 mM., were oxidized at 16° C. in 3.2 ml. of solution containing 0.05 mM. sodium periodate and 0.042 mM. sodium bicarbonate and saturated with carbon dioxide according to the procedure developed by Perlin (16) using a Warburg apparatus to follow the liberation of carbon dioxide. The results of typical runs are plotted in Fig. 1. Only negligible

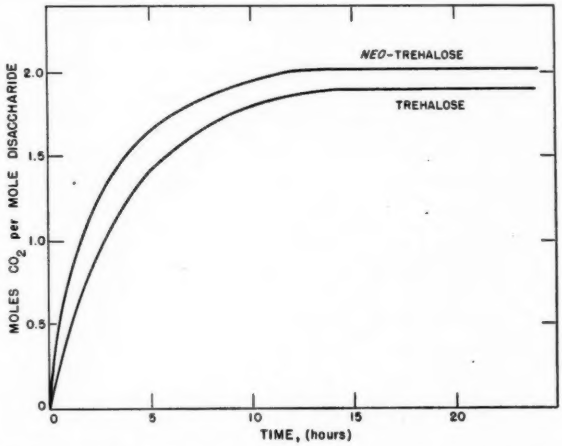

FIG. 1. The rates of liberation of formic acid on periodate oxidation of trehalose and *neo*-trehalose measured by the method of Perlin (16).

amounts of formaldehyde could be detected in the oxidation mixture after 24 hr. reaction time using the chromotropic acid reagent.

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SULPHUR ISOTOPE EFFECTS IN THE BISULPHITE ADDITION REACTION OF ALDEHYDES AND KETONES

II. BOND-FORMATION EFFECT[1]

By W. A. Sheppard,[2] R. F. W. Bader,[3] and A. N. Bourns

ABSTRACT

The relative rates of formation of C^{12}–S^{32} and C^{12}–S^{34} bonds in the bisulphite addition reaction of heptanal, benzaldehyde, anisaldehyde, and 2-heptanone have been measured and found to approximate unity. This result has been interpreted in terms of the Bigeleisen treatment of isotope effects in unidirectional processes.

INTRODUCTION

During the past few years a number of papers have appeared dealing with the fractionation of the isotopes of the lighter elements, other than hydrogen, due to differences in reaction rates. Attention has been given chiefly to reactions in which a bond associated with the isotopic atom is broken in the rate-determining step, although a simultaneous bond-rupture and bond-formation mechanism has been proposed to account for the isotope effects observed in the deammonation of phthalamide (9) and the pyrolysis of barium adipate (3). Certain complex reactions in which the initial step is probably a reversible bond-formation process have also been investigated (10, 6), but as yet no isotope effect studies have been reported for a simple one-step bond-formation reaction.

In a previous communication from this laboratory (8), equilibrium constants of 1.010 to 1.021 were reported for the $S^{32}:S^{34}$ isotopic exchange reaction between bisulphite ion and the bisulphite-addition products of a number of aldehydes and ketones. These results were considered as evidence in support of the sulphonic acid structure of the addition compounds. The present paper deals with an extension of these studies in which the isotopic fractionation arising from the difference in reaction rates of light and heavy sulphur in the forward reaction *alone* has been determined. If, as seems likely, the rate-determining step of the addition reaction is the attack of bisulphite ion on the carbonyl carbon, the results give a measure of the sulphur isotope effect in the formation of a carbon–sulphur bond.

The bisulphite-addition reaction is readily reversible and isotopic equilibrium between bisulphite ion and the addition product is quite rapidly established. Although it was possible to reduce the contribution of the reverse reaction to the observed fractionation by removing the precipitated addition product as rapidly as possible from the reaction system, conditions which give a strictly unidirectional process could not be achieved. However, the isotope effect for the addition reaction could be determined with reasonable accuracy by

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Contribution from the Department of Chemistry, Hamilton College, McMaster University, Hamilton, Ontario.
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[3] *Undergraduate student.*

measuring the fractionation after varying short reaction periods and extrapolating to zero time.

Bisulphite ion was used in a very large excess in all experiments and no significant change in the isotopic ratio of this reactant, therefore, occurred during the addition reaction. It follows that the extent of fractionation at any time t is given, to a very close approximation, by the quotient $\left(\frac{S^{32}}{S^{34}}\right)_{\text{prod.}} \Big/ \left(\frac{S^{32}}{S^{34}}\right)_{HSO_3^-}$, where $\left(\frac{S^{32}}{S^{34}}\right)_{HSO_3^-}$ is the ratio of the two sulphur isotopes in the original sodium bisulphite reactant and $\left(\frac{S^{32}}{S^{34}}\right)_{\text{prod.}}$ is the corresponding ratio in the addition product removed from the reaction system at time t. Extrapolation to zero time of the plot of this quotient against time gives the specific rate constant ratio, k^{32}/k^{34}, for the reaction of light and heavy species of bisulphite ion.

RESULTS

In Fig. 1 are shown $\left(\frac{S^{32}}{S^{34}}\right)_{\text{prod.}} \Big/ \left(\frac{S^{32}}{S^{34}}\right)_{HSO_3^-}$ values for four bisulphite ion–carbonyl systems determined at 25°C. and plotted as a function of time. Equilibrium values previously reported (8) are also indicated.* The standard deviation of the isotopic ratios represented by the individual points in this figure was of the order of 0.1%.

The extrapolated values for the isotopic ratios shown in the figure are subject to considerable uncertainty owing to limitations in the precision of the mass spectrometer analyses and the experimental difficulty in obtaining points at very short reaction times. Nevertheless, in the heptanal, anisaldehyde, and 2-heptanone systems, the conclusion that the reaction rates of the two isotopic species of bisulphite ion differ by no more than 0.2% would appear to be justified. With benzaldehyde, the isotope effect is somewhat larger and it can definitely be concluded that the reaction of $HS^{32}O_3^-$ is favored.

It should be noted that the addition reaction was very rapid under the conditions used in obtaining these results, particularly in the case of heptanal and benzaldehyde. In fact, with these compounds, almost complete precipitation of the addition product usually occurred in less than one minute. The possibility, therefore, that the rate-determining process might be the diffusion of bisulphite ion through the aqueous solution to the droplets of the insoluble carbonyl compound must not be overlooked. For this reason, a number of experiments with heptanal were made in which the rate of reaction was greatly reduced by diluting the aldehyde with benzene. From the results given in Table I, it is apparent that, even under these conditions, isotopic fractionation was extremely small. It may therefore be concluded that for the reaction of heptanal with sodium bisulphite the rate constant ratio, k^{32}/k^{34}, is close to unity and probably falls within the range 0.999–1.001.

**In order to compare the fractionation observed under equilibrium conditions with the rate-constant ratios, k^{32}/k^{34}, the equilibrium values are expressed as the reciprocals of the equilibrium constants previously reported.*

TABLE I
ISOTOPE EFFECT IN THE REACTION OF SODIUM BISULPHITE WITH HEPTANAL DILUTED WITH BENZENE (25°C.)
(20 ml. saturated sodium bisulphite, 20 ml. benzene)

Run No.	Heptanal, ml.	Reaction time, sec.	% yield (based on RCHO)	$\left(\frac{S^{32}}{S^{34}}\right)_{prod.} / \left(\frac{S^{32}}{S^{34}}\right)_{HSO_3^-}$
D_I	1.5	30	1.4	0.9996
D_{II}	1.5	30	1.4	0.9982
B_{III}	3.0	15	7.3	0.9982
C_I	3.0	30	19.5	0.9995
C_{IV}	3.0	300	38.6	1.0008

EXPERIMENTAL

Reagents

The source and purity of all reagents were as previously reported (8).

Preparation of the Addition Compounds

A. *Without Diluent*

To a saturated aqueous solution of sodium bisulphite, containing 5.15 moles of bisulphite per liter of solution, was added the carbonyl compound in the quantity necessary to give a bisulphite to carbonyl molar ratio of 10 : 1. The mixture was shaken vigorously from the time of mixing for periods ranging from the point of first precipitation of the addition product up to a total reaction time of four to six minutes. With the exception of the product from anisaldehyde, the addition compounds started to separate within one-half minute and, in the case of heptanal and benzaldehyde, the reaction was essentially complete a few seconds after the appearance of the first precipitate. The product was rapidly removed by suction filtration, washed with ethanol and then with ether, and dried.

B. *With Benzene Diluent*

Heptanal (1.5 or 3.0 ml.) was diluted with 20 ml. of thiophene-free benzene and the solution then mixed with 20 ml. of saturated aqueous sodium bisulphite. After vigorous shaking for the desired reaction period, the addition product was removed, washed, and dried.

Determination of Isotopic Ratios

Sulphur dioxide samples for mass spectrometric analysis were prepared from the addition compounds by the method previously described (8).

The samples from the addition product obtained in the reaction carried out in the absence of the diluent were analyzed in a 90° direction focusing Nier type mass spectrometer. The same instrument, but equipped for simultaneous collection, was used for the samples prepared from the product of the benzene diluted reaction medium. Details of the mass spectrometer measurements are found in the earlier paper (8).

DISCUSSION

The effect of isotopic substitution on rates of chemical reactions has recently been treated theoretically by Bigeleisen (1, 2), who has developed the following

equation for the calculation of rate constant ratios:

$$\frac{k_1}{k_2} = S\left(\frac{m_2^*}{m_1^*}\right)\left[1 + \sum_i^{3n-6} G(u_i)\,\Delta u_i - \sum_i^{3n'-6} G(u_i^{\ddagger})\,\Delta u_i^{\ddagger}\right]$$

where the subscripts 1 and 2 refer to the light and heavy isotopic molecules, respectively, S is a statistical factor, m^* is an effective mass of the molecule along the reaction coordinate, $\Delta u_i = (hc/kT)(\omega_{1i} - \omega_{2i})$, $G(u_i)$ is a function previously defined by Bigeleisen and Mayer (4), and ‡ refers to the activated complex. S is unity except in reactions in which there are two or more identical atoms of the isotope in question in the molecule. The factor $(m_2^*/m_1^*)^{\frac{1}{2}}$, which gives the ratio of the number of molecules in the transition state undergoing reaction per unit time, may be calculated as the reduced mass of the two atoms connected in the bond being broken or formed. The quantity in the square brackets describes quantitatively the zero point energy effects.

In reactions involving the rupture of a bond connected with the isotopic atom, the molecule is more "tightly bound" in the initial state than in the activated complex,

i.e., $$\sum_i^{3n-6} G(u_i)\,\Delta u_i > \sum_i^{3n'-6} G(u_i^{\ddagger})\,\Delta u_i^{\ddagger}.$$

The zero point energy term is therefore greater than unity and its effect on the relative reaction rates is in the same direction as the reduced mass term.

For reactions in which the isotopic atom forms a new bond without any appreciable weakening of other bonds involving this atom, however, one would expect this atom to be more tightly bound in the activated complex than in the initial state, i.e.,

$$\sum_i^{3n'-6} G(u_i^{\ddagger})\,\Delta u_i^{\ddagger} > \sum_i^{3n-6} G(u_i)\,\Delta u_i.^*$$

The zero point energy term of the Bigeleisen expression would then be less than unity and would tend to cancel the term involving the reduced masses. This interpretation would appear to account qualitatively at least for the approximately zero sulphur isotope effect in the bisulphite addition reaction.

It is of interest to attempt a more quantitative theoretical analysis of the isotope effect in this bond formation reaction. If one assumes that the vibrational frequencies of all bonds other than the bond being formed are unchanged in going from initial state to activated complex, then the reaction can be treated as the formation of the hypothetical C–S molecule from separated atoms. The term

$$\sum_i^{3n-6} G(u_i)\,\Delta u_i$$

is then zero. Some model must be assumed for the activated complex in order to evaluate

$$\sum_i^{3n'-6} G(u_i^{\ddagger})\,\Delta u_i^{\ddagger},$$

**On the other hand, isotope effect studies on the hydrolysis of esters* (10) *and reaction of dimedon with formaldehyde* (7) *suggest that the initial state term is greater than the activated complex term in bond formation at the carbonyl carbon. In these reactions, however, bond formation is clearly accompanied by the weakening of other bonds; a π bond is broken and the hybridization of carbon in the three σ bonds is changed from sp^2 to sp^3.*

and it is convenient to consider that the new bond is completely formed, in other words, that the vibrational frequencies of the C–S bond in the activated complex are the same as in the product. Using a wave number of 760 cm.$^{-1}$ for the C^{12}–S^{32} bond (5, 7) and 754 cm.$^{-1}$ for the C^{12}–S^{34} bond (calculated from the relation of the reduced masses), one obtains a k^{32}/k^{34} ratio of 1.001 at 25°C., compared to the experimental values of approximately 0.999 to 1.003 for the four systems studied (see Fig 1).

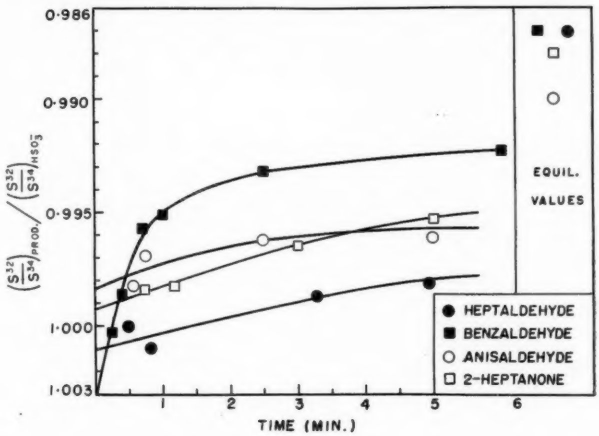

FIG. 1. Variation of $\left(\frac{S^{32}}{S^{34}}\right)_{\text{prod.}} / \left(\frac{S^{32}}{S^{34}}\right)_{HSO_3^-}$ ratios with reaction time.

Somewhat poorer agreement between calculated and experimental values would be anticipated for the reaction of bisulphite ion with lower molecular weight carbonyl compounds such as acetone. Although the unidirectional effect could not be determined experimentally for such systems owing to the much greater solubility of the addition product in saturated sodium bisulphite, their lower equilibrium values, $1/K$, for isotopic exchange (8) would suggest a k^{32}/k^{34} ratio of several tenths of a per cent less than unity. The agreement with the calculated value, nevertheless, is as good as could be expected bearing in mind the assumptions made in the calculations and the model chosen for the transition state.

The results demonstrate that this treatment permits a semiquantitative prediction of the magnitude of isotope effects in simple bond-formation processes.

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THE REACTION OF ACTIVE NITROGEN WITH PROPANE[1]

By M. Onyszchuk,[2] L. Breitman,[3] and C. A. Winkler

ABSTRACT

The reaction of nitrogen atoms with propane has been found to produce hydrogen cyanide as the main product, together with smaller amounts of acetylene, ethylene, and ethane, which were recovered at all propane flow rates. Complete consumption of nitrogen atoms was not attained at any propane flow rate used at 63°C., but was attained at 250°C. for ratios of propane to nitrogen atoms greater than 1.3. An activation energy of 5.6 ± 0.6 kcal. and a steric factor between 10^{-2} and 10^{-3} was estimated from second order rate constants.

The reaction of active nitrogen with propane has been discussed briefly in a recent review of active nitrogen – hydrocarbon reactions (13). A detailed examination of the reaction products and their dependence on propane flow rate is reported in the present paper. As before, it is assumed that the chemically reactive species in active nitrogen is atomic nitrogen (3, 4).

EXPERIMENTAL

The apparatus used in this investigation was similar to that described in earlier papers from this laboratory (3, 4). Preliminary experiments showed that hydrogen cyanide was the major product, and that ethylene, acetylene, ethane, and methane were formed in much smaller quantities.

The vapor pressure – temperature relations for acetylene and propane are not sufficiently different at low temperatures to allow their fractionation in the LeRoy distillation apparatus used (6). Therefore, a portion of the unreacted propane was codistilled with ethylene and acetylene at −140°C. until the equilibrium vapor pressure decreased from that of the mixture to that of propane at this temperature. Analysis with a mass spectrometer gave the composition of this combined C_2–C_3 hydrocarbon fraction.

The remaining propane fraction, containing only a trace of acetylene, was separated from hydrogen cyanide by distillation at −120°C. Hydrogen cyanide was distilled at −70°C. and condensed on the surface of 10 ml. of 1 *N* potassium hydroxide which had been previously degassed and frozen in a detachable trap immersed in liquid nitrogen. The trap, closed with a stopcock, was removed and its bottom end plunged into hot water. This melted the alkali solution, which then dissolved the hydrogen cyanide before it could melt and polymerize. Titration of the resulting solution with standard silver nitrate gave the cyanide content.

Analysis of noncondensable products, methane and hydrogen, was not made.

The molecular nitrogen flow rate was maintained constant at 5.83×10^{-5} mole per sec.; this gave a pressure of 1.35 ± 0.02 and 1.42 ± 0.01 mm. of

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[2] *Holder of a National Research Council Studentship.*
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mercury at 63 ± 3° and 250 ± 5°C. respectively. Experiments were made at each temperature with propane flow rates ranging from 5×10^{-7} to 2×10^{-5} mole per sec.

From 15 experiments with ethylene at 100° and at 260°C., under experimental conditions corresponding to complete removal of the available nitrogen atoms (11), the atomic nitrogen flow rate was estimated to be $5.20 \pm 0.50 \times 10^{-6}$ mole per sec.

RESULTS AND DISCUSSION

The results of the investigation are summarized in Fig. 1. Hydrogen cyanide accounted for 90–97% of the propane consumed and the remainder was recovered as ethylene, acetylene, and ethane. The average carbon and hydrogen balances were 101% and 92% respectively.

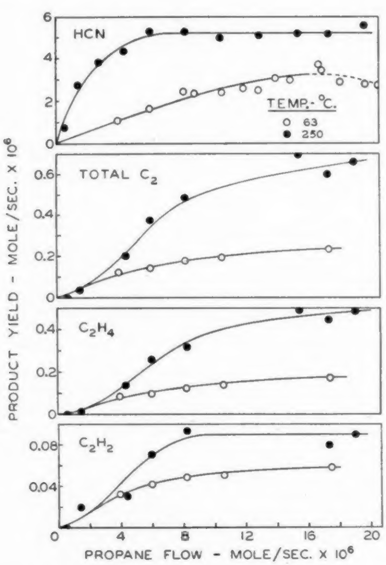

FIG. 1. Rate of formation of various products in the nitrogen atom – propane reaction, as a function of propane flow rate.

The yield of hydrogen cyanide from the reaction at 63°C. increased gradually with increasing propane flow rate, and appeared to pass through a maximum without complete consumption of the nitrogen atoms available. The presence of the maximum may result, in part, from dilution effects which reduce the reaction time significantly at high propane flow rates. Moreover, under these conditions the reaction flame was localized at the top of the reaction vessel where the surface to volume ratio is relatively large and loss of nitrogen atoms or nitrogen atom – propane complexes at the surface might lead to the observed decrease in hydrogen cyanide production.

For the reaction at 250°C., on the other hand, the yield of hydrogen cyanide remained constant at 5.2×10^{-6} mole per sec. beyond a critical propane flow rate of about 7×10^{-6} mole per sec. This value corresponds to the average atomic nitrogen flow rate determined from the ethylene experiments. It may be concluded that when the flow rate of propane exceeds the nitrogen atom flow rate by a factor of 1.3 or greater, the reaction proceeds to complete removal of the available atomic nitrogen.

The curves representing production of C_2 hydrocarbons (mainly ethylene and acetylene) offer further support to the conclusion that nitrogen atoms are completely consumed at 250° but not at 63°C. Since ethylene and acetylene react rapidly with nitrogen atoms, a continued increase in the amounts of these hydrocarbons would be expected above the critical propane flow rate. This was realized experimentally for ethylene, but only at the high reaction temperature. On the other hand, if nitrogen atoms are available for reaction at all propane flow rates, the curve for C_2 hydrocarbon production should parallel that for hydrogen cyanide formation. This appears to be true for the reaction at 63°C.

Of particular significance was the recovery of ethylene and acetylene in the region of incomplete consumption of nitrogen atoms. The reaction of nitrogen atoms with these unsaturates is about ten times more rapid than the reaction with propane, if it is assumed that the initial attack of a nitrogen atom on a hydrocarbon molecule is rate controlling. Since ethylene, acetylene, and propane would be expected to compete for nitrogen atoms according to their relative reactivities, the recovered unsaturates should represent only a fraction of the total amounts formed. Conservative calculations indicate that most of the hydrogen cyanide was probably derived from ethylene and acetylene formed by the primary attack of nitrogen atoms on propane.

The general reaction mechanism which has been tentatively suggested for the paraffin hydrocarbon – nitrogen atom reaction (13), and which appears to be satisfactory for the ethane reaction (3), cannot adequately explain the presence of ethylene and acetylene among the products of the propane reaction. The recovery of these unsaturates in appreciable amounts in the region of excess nitrogen atoms implies their formation in a primary reaction step, rather than from secondary reactions involving hydrogen atoms and free radicals. A number of possible reactions might be suggested, but many of these are energetically unfavorable while others involve the improbable formation of "hot" radicals from the collision complex. A thermochemically favorable reaction of a type by which ethylene might be formed by decomposition of the propane–nitrogen atom collision complex would be

$$N + C_3H_8 \rightarrow \text{Collision complex} \rightarrow HCN + CHCH_3 + H_2 + H. \qquad [1]$$

The ethylidene radical previously postulated in the nitrogen atom – propylene reaction (10) and in other reactions (1, 2) is thought to transform rapidly to ethylene,

$$CH_3CH \rightarrow CH_2{=}CH_2$$

An alternative primary step might produce acetylene directly by a similar exothermic reaction,

$$N + C_3H_8 \rightarrow \text{Collision complex} \rightarrow HCN + C_2H_2 + 2H_2 + H. \quad [2]$$

Nitrogen atom reaction with the ethylene and acetylene produced by reactions [1] and [2] could occur as outlined in previous papers (11, 12).

Both reactions [1] and [2] are admittedly incompatible with the Rice–Teller principle of least motion (8). However, this principle has been applied to processes that involve energies of about 100 kcal. or less, while in the nitrogen atom reactions, the high energy of formation of the $C \equiv N$ bond (170–200 kcal.) is effectively released within the reaction complex and might result in considerably more intracomplex rearrangement than would otherwise be expected.

The small quantities of ethane detected only in the experiments at 250°C. probably resulted from the hydrogenation of ethylene by atomic hydrogen (7).

Second order rate constants were calculated for the propane–nitrogen atom reaction in a manner similar to that previously outlined for the ethane reaction (3). In Table I are recorded the data obtained for experiments corresponding

TABLE I
DATA USED FOR THE CALCULATION OF SECOND ORDER RATE CONSTANTS

Propane flow	HCN formed	Reaction time, sec.	Ratio of propane* consumed to at. N	k, l.mole.$^{-1}$sec.$^{-1}$ $\times 10^{-5}$	
Mole.sec.$^{-1}$ $\times 10^6$				Streamline flow	Turbulent flow
Temperature = 63 ± 3°C.					
3.92	1.12	0.322	0.375	0.772	2.46
5.97	1.64	0.312	0.391	0.880	2.89
8.21	2.44	0.302	0.381	1.12	4.33
8.83	2.37	0.299	0.378	1.00	3.83
10.6	2.42	0.292	0.387	0.915	3.43
12.0	2.58	0.286	0.357	0.844	3.09
13.0	2.48	0.282	0.385	0.820	3.52
14.1	3.07	0.278	0.378	1.05	4.68
15.5	3.03	0.273	0.375	0.961	4.23
16.7	3.45	0.269	0.378	1.16	5.75
16.8	3.74	0.268	0.381	1.41	7.50
Temperature = 250 ± 5°C.					
0.473	0.777	0.230	0.333	10.2	50.0
1.42	2.77	0.227	0.341	19.9	150
2.73	3.83	0.222	0.352	16.8	133
4.43	4.37	0.217	0.381	13.8	129

**The amount of propane consumed was calculated from the total amount of HCN and C_2 hydrocarbons produced.*

to incomplete consumption of nitrogen atoms and used for the calculation of second order rate constants when both streamline and turbulent flow conditions are assumed. The average values of the rate constants, together with the corresponding activation energies, E, and steric factors, P, in the expression $k = PZe^{-E/RT}$ are shown in Table II. The collision number, Z, was calculated using collision diameters of 3.0 Å and 4.2 Å for atomic nitrogen (5) and pro-

TABLE II

KINETIC CONSTANTS FOR THE NITROGEN ATOM – PROPANE REACTION

Flow condition assumed	Temp., °C.	k, $\text{l.mole.}^{-1}\text{sec.}^{-1}$	P	E, kcal.
Streamline	63	9.94×10^4	9.1×10^{-4}	5.1
	250	1.52×10^6		
Turbulent	63	4.16×10^5	2.1×10^{-2}	6.2
	250	1.16×10^7		

pane (9) respectively. Actual flow conditions within the reaction vessel probably lie somewhere between the two extremes assumed.

ACKNOWLEDGMENTS

Grateful acknowledgment is made to Dr. R. A. Back, who concurrently investigated the nitrogen atom reaction with the butanes, for many helpful discussions of the reaction mechanism. The authors are also indebted to Dr. H. I. Schiff of this department for mass spectrometer analyses.

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ADDITION COMPOUNDS OF THE MOLECULAR HALIDES

III. THE TRICHLORIDES AND PENTACHLORIDES OF PHOSPHORUS, ARSENIC, ANTIMONY, AND BISMUTH WITH TRIETHYLAMINE[1]

By W. R. Trost

ABSTRACT

Monoaminates of the trichlorides and pentachlorides of phosphorus, arsenic, antimony, and bismuth have been prepared, as well as triaminates of the trichlorides of phosphorus and arsenic and mixed polyaminates of the remaining chlorides. The co-ordinate valences and possible structures of the compounds are related to a model that depends on the geometry of the molecular halide and on the outer orbitals of the atoms in it.

INTRODUCTION

The possibility that the $(n+1)s$, nd, $(n+1)p$ orbitals are significant bonding factors carries with it definite implications concerning the structures and the reactions of inorganic compounds. The systems provided by saturated molecular halides with independent donor groups are particularly suited to a study of the role and function of these outer orbitals. Addition reactions between the Group V halides and tertiary amines would be expected if outer orbitals are effective electron acceptors. Differences from the Group IV tetrahalides (1), because of the lone-pair on the Group V atoms and the less symmetrical structures of the tri- and pentachlorides, may occur.

EXPERIMENTAL

The liquid chlorides (PCl_3, $AsCl_3$, $SbCl_5$) were purified by fractionation; the solid chlorides (PCl_5, $SbCl_3$, $BiCl_3$) by sublimation; and triethylamine, after treatment with anhydrous potassium hydroxide, by fractionation. Measured volumes of individual liquid chlorides and triethylamine were mixed together by consecutive condensation into a flask, at $-78°C$. The mixtures were brought to room temperature, while being magnetically stirred. Then volatile products were removed from the mixture by condensation into a volumetric flask, at $-78°C$. The vapor pressure of the mixture, at 16°C., was plotted with reference to the mole fraction remaining in the mixture. When the vapor pressure had fallen to zero, at 16°C., the temperature of the mixture was steadily raised until phase change or thermal decomposition began. The products above 16°C. were collected separately from the liquid condensates recovered at 16°C.

All operations, from purification to thermal decomposition, were carried out in an all glass vacuum system that had been flamed, and was filled with dried nitrogen when a procedure required it. The solid chlorides were weighed outside the vacuum system, the procedure with them being otherwise the same.

Mole ratios in the mixtures were calculated from density and volume for the liquids. Liquid volumes were measured directly in the vacuum system in

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the graduated tubes that were used to supply to, and to receive from, the mixture. The products recovered from the mixtures were identified, when they were unchanged chloride or amine, by vapor pressure or melting point. The products of the thermal decomposition, however, were not identified, if they were neither amine, chloride, nor amine hydrochloride, although qualitative tests for amine, chloride, and Group V element were generally completed.

RESULTS

The Trichlorides

The condensation of phosphorus trichloride, or arsenic trichloride, into excess triethylamine at $-78°$ immediately produces a white solid substance. When one mole of trichloride has been added to six moles of amine, no free liquid can be observed in the mixture. The vapor pressure of the mixture, 48 mm. at 16°C., is, however, normal for that of liquid amine at the same temperature. As the vapor is condensed out of the mixture, the white solid cracks and shrinks, and the vapor pressure falls slowly (Table I), until very

TABLE I

VAPOR PRESSURE OF TRIETHYLAMINE AS A FUNCTION OF THE MOLE RATIO OF AMINE TO TRICHLORIDE

Chloride	Vapor pressure of triethylamine in mm. Hg					
	Mole ratio					
	6/1	5/1	4/1	3/1	2/1	1/1
PCl_3	48	47	30	0		
$AsCl_3$	48	48	31	8	0	
$SbCl_3$	48	48	47	47	46	0
$BiCl_3$	48	47	45	40	20	0
PCl_5 (*a*)	49	45	35	30	0	
PCl_5 (*b*)	48	48	40	35	36	0
$SbCl_5$	48	49	48	48	48	0

Temperature = 16°*C.*

(*a*) *After two hours.*
(*b*) *After two days.*

nearly three moles of amine have been recovered. Then the vapor pressure abruptly vanishes, even though the temperature of the mixture is raised from 16° to 200°C. The composition of the mixtures from which all volatile amine has been removed are shown in Table II. They correspond to the triaminates, $PCl_3.3ET_3N$, $AsCl_3.3ET_3N$, and are stable, white, powders at room temperature. They begin to decompose, in vacuum, at 50° to 60°, a colorless liquid with no measurable vapor pressure condensing out of the solid mixture, which is itself developing yellow colors. At about 150°, white solids begin to sublime out of the residue; at 200°, the residue, which may have become quite orange, has been entirely transformed into the white sublimate and colorless liquid. The two products, on mixing, reproduce the yellow colors observed in the mixture in the course of its thermal decomposition. From qualitative tests, each product contains chlorine, amine, and phosphorus or arsenic.

TABLE II

COMPOSITION AND STABILITY OF ADDITION COMPOUNDS

Compound	Experimental data			
	Mole ratio $\frac{NR_3}{MX_a}$	Softening temperature, °C.	Transitions	Decomposition temperature, °C.
$PCl_3.Et_3N$	1.2	*ca.* 0	20°, -2 PCl_3 to triaminate	
$PCl_3.3Et_3N$	3.1			50
$AsCl_3.Et_3N$	0.85	30		
$AsCl_3.3Et_3N$	2.8			60
$SbCl_3.Et_3N$	0.96	50	40°, to black glass	
$BiCl_3.Et_3N$	1.1	210	140°, to gray glass	
$PCl_5.Et_3N$ (*b*)	1.1	200	170°, to black powder	115
$PCl_5.n\ Et_3N$ (*a*)	2.5	175	175°, to black liquid	125
$SbCl_5.Et_3N$	1.2	60		125
$SbCl_5.n\ Et_3N$	2.4	70		110

The addition of triethylamine to excess phosphorus trichloride at −78°C., or to arsenic trichloride at 0°C., produces oily liquids and transparent, colorless low melting glasses, as the mole ratio changes. One mole of amine in five moles of phosphorus trichloride is a transparent glass at −78°C., but shows the normal vapor pressure of phosphorus trichloride, and can be magnetically stirred, at 16°C. As phosphorus trichloride vapors are removed, the stirring becomes more difficult and at mole ratios of about 1:1 the vapor pressure begins to fall, rather abruptly, and continues to fall more slowly, as the gel transforms into a white powdery solid, with the experimental formula, $PCl_3.2.8\ Et_3N$. The latter compound, in its behavior at higher temperatures, is identical with the triaminate recovered from mixtures rich in amine.

Amine in excess arsenic trichloride produces mixtures that differ from those with phosphorus trichloride in that the softening temperatures of the glasses are higher, and the transformation to the triaminate is not complete. The experimental compositions and softening temperatures of what will be called the monaminates of phosphorus and arsenic trichlorides are shown in Table II.

The trichlorides of antimony and bismuth are solid compounds. No changes are observed in them when triethylamine is added at −78°. On warming to room temperature, the solids slowly expand to volumes many times the original one, but liquid amine remains visibly unassociated if the amine to trichloride ratio is greater than 6 : 1. On removing the amine from the mixture, although the solid shrinks, the vapor pressure very nearly remains normal until it drops to zero at about a 1 : 1 composition in the mixture (Table I). On warming, the white solids turn black and begin to melt, but no vapor pressure is developed. The aminate of arsenic trichloride turns black at 40° and begins to soften at about 50°, turning into a red-brown liquid at about 100°, without any signs of chemical decomposition. The monoaminate of bismuth trichloride transforms to a gray glassy solid at about 140° and begins to soften at about 210°. Once formed, the monoaminates remain glassy solids, even at low temperatures.

The Pentachlorides

Liquid triethylamine, condensed into solid phosphorus pentachloride at $-78°C.$, disappeared in the formation of a new white solid that looked wet if the amine excess was greater than 6 to 1. The solids cracked and shrank, and the vapor pressure dropped slowly, as amine was removed (Table I). In two mixtures, one of which (PCl_5 *a*) had stood at room temperature for two hours, the other (PCl_5 *b*) for two days, the products remaining when all volatile amine had been removed had the experimental compositions, respectively, of $PCl_5.2.5\ Et_3N$ and $PCl_5.1.1\ Et_3N$. The former was white, the latter yellow. The thermal decompositions of the two aminates differed in the relative amounts of products, but were otherwise rather similar. Both compounds were unchanged at 115°C., but then began to decompose. The products were a gas volatile at $-78°$, a colorless nonvolatile liquid, and, from the monoaminate only, a solid sublimate. Both compounds were yellow at this temperature, turned black rather abruptly at 170–175°, and soon after began to soften (Table II).

Liquid antimony pentachloride also formed mixed products when mixed with triethylamine at 0°C. The addition of amine to pentachloride was accompanied by the immediate formation of colored compounds which, at about a 1 to 1 mole ratio, had become a glass-like, almost black solid. No further change occurred upon the addition of more amine, perhaps because stirring was not possible. Experimentally, the monoaminate had the composition, $SbCl_5.1.2\ Et_3N$. It began to soften at about 60° and to decompose (a gas volatile at $-78°C.$) above 100°C. (Table II). The addition of antimony pentachloride to excess triethylamine produced, in addition to the noncrystalline black solid, a white flocculent solid. The vacuum system technique did not permit the separate preparation of these compounds. The mole ratio of the mixture, $SbCl_5.2.4\ Et_3N$, has therefore no specific significance. It might be mentioned that the addition of a petroleum ether solution of antimony pentachloride to excess triethylamine produces only a white solid.

DISCUSSION

The Group V elements, like the Group IV elements, combine with halogens to form compounds in which all valence orbitals contain electron pairs. These molecular halides are nevertheless still able to form addition compounds with donor groups like triethylamine. The co-ordinate bonds presumably responsible for such intermolecular combinations require the presence of accepting orbitals on the molecular halide. However, only outer orbitals are vacant; it becomes necessary, therefore, to ascribe to them the property of reaction with donor electron pairs, if the addition compounds are to be explained.

Each atom in the molecular halide is expected to contribute to the molecular accepting orbitals to an extent dependent on the electronegativities and energy levels of its outer orbitals. The numerous atomic orbitals then combine with one another, through the geometry of the molecule, to provide the molecular accepting orbitals the molecular halide shows in its addition compounds. Perhaps the detailed problem involved in these combinations can be solved.

However, the geometry of the molecular halide depends only on the orbital configuration of the nonhalogen atom. It is also the point of highest symmetry in the molecule, which is a distinct consideration in the formation of the molecular accepting orbital. The nonhalogen atom may therefore itself largely determine the structures and valences shown in the addition compounds of these molecular halides. The simplification permits a specific discussion of the compounds, particularly in a series in which the halogen remains the same. In the trichlorides of phosphorus, arsenic, antimony, and bismuth, the outer orbitals are the $(n+1)s$, $(n+1)p$, nd, $(n-1)f$ orbitals of the Group V elements. As the outer s orbital is stabler than any others a 1 : 1 compound is a possibility for all the Group V chlorides. More extensive addition of donor groups, in which s, p, d hybrid orbitals are used, are also possible, particularly with the hybrid configurations that reflect the structure of the molecular halide (1). The increase in the stability of the orbitals, from phosphorus to bismuth, as the energy separation between the valence and the outer orbitals is diminished, is counterbalanced by a decrease in their accepting properties as the electronegativity of the Group V atoms becomes smaller.

The presence of an unshared electron pair on the Group V atom, if it occupies a directed orbital, would have definite effects on the addition compounds of the trihalides. The bond angles in the trichlorides of phosphorus, arsenic, and antimony are all greater than 100°, and indicate that the electron pair is in the fourth sp^3 orbital about those atoms. As long as this position is occupied a tetrahedral structure for the monoaminate is not possible, and looser, less distinctive 1 : 1 associations are implied. In contrast, the triaminates may have definite structures. Two related possibilities arise. In each, the same hybrid from the stabler outer orbitals, the $(n+1)s$ and the nd, is assigned to the coordinations. The hybrid most suited to the structure of the trichloride is the planar d^2s. It puts three amines in three identical positions around the molecular halide. Each amine is located between and above two chlorine atoms, in the plane perpendicular to the unshared sp^3 orbital. The alternative structure occurs if the lone-pair on the nonhalogen shifts from an sp^3 to an s orbital. The three bonds in the trichloride therefore become p^3. In combination with the d^2s co-ordinations, an octahedral type p^3d^2s structure for the triaminate is achieved. Either alternative implies a solid structure of perhaps chain or layer type, and therefore explains the valence and state of the triaminates.

Though the triaminates were definite compounds with PCl_3 and $AsCl_3$, only indirect and visual evidence for polyaminates were obtained with $SbCl_3$ and $BiCl_3$. That is, the triaminates were the more stable compounds with the liquid trichlorides, while the monoaminates were with the solid trichlorides. It is possible that this comparison is partly unreal, in the sense that it may reflect the experimental method, rather than a physical property; that is, the solid halides could not be added to the amine as isolated molecules. Nevertheless, the co-ordinations in a layer structure like $BiCl_3$ are always competitive with those involved in the addition of amine. For this reason the elimination of amine is an easier process from a solid chloride than from a liquid chloride, if the amine co-ordinations are similar in both cases. Apart from this, it seems

likely that the bismuth monoaminate may have achieved extra stability through hybridization. Its lone-pair is most likely, of the Group V elements, to be undirected, physical evidence coming from its (6×2) layer structure and from its ionic valence. Then the monoaminate could have the more symmetrical p^3s structure, with the chlorines and the amine using equivalent bismuth orbitals. Transitions from white powders to dark glass-like compounds were observed in the monoaminates of antimony and bismuth at 40° and 140° respectively.

Oddly enough, perhaps, monoaminates and triaminates appear to be the best possibilities for the pentachlorides as well. The monoaminate uses the $(n + 1)s$ orbital to make the glass-like compounds, observed with antimony pentachloride, and at higher temperatures perhaps with phosphorus pentachloride. An alternative for the monoaminate is the combination of an nd orbital with the sp^3d pentachloride to make an octahedral sp^3d^2 monoaminate. One monoaminate of phosphorus pentachloride was a yellow powder, up to 115° (Table II).

The next definite addition compound, in the model, uses outer d^2s orbitals, and just fits three amines into the three equivalent hollows of the trigonal bipyramid pentachloride molecule. It was not, however, possible to prepare the polyaminates of these compounds in a pure state. The observed mole ratios of 2.5 in mixtures can only indicate that polyaminates occur, and do not imply that a real triaminate has been approximated. It is to be remembered that PCl_5 has a solid structure that combines PCl_4 with PCl_6 units in three dimensions. The nonintegral mole ratio may imply that these units add different numbers of amines, as the solid structure changes, and that further exchanges occur between them before aminated PCl_5 units are obtained.

It has not been possible from the data to draw any conclusions about the relative strengths of the amine co-ordinations with the series of Group V halides. This is partly because thermal decomposition precedes vaporization and dissociation for these compounds, and partly because the properties of the condensed phases depend in an important way on other structural factors. However, the occurrence of stable aminates with all of the chlorides does imply that at least two factors are involved in the additions, particularly as the triaminates were most marked with PCl_3, and the monoaminates with $BiCl_3$.

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THE ACETYL GROUP MIGRATIONS IN D-GLUCOSE DIETHYL THIOACETYL TETRAACETATE[1]

By R. U. Lemieux and H. F. Bauer

ABSTRACT

The D-glucose diethyl thioacetal tetraacetate prepared by Wolfrom and associates both by detritylation of 6-*O*-trityl-D-glucose diethyl thioacetal tetraacetate and mercaptalation of 2,3,4,6-tetra-*O*-acetyl-β-D-glucose was obtained by direct acetylation of D-glucose diethyl thioacetal with acetic anhydride and sodium acetate. Methylation of the tetraacetate followed by deacetylation and demercaptalation gave only 2-*O*-methyl glucose and methyl β-D-glucopyranoside.

Acetylation of D-glucose diethyl thioacetal (I) with acetic anhydride and sodium acetate on the steam bath for a half hour results in the formation of a tetra-*O*-acetyl derivative (II) which can be readily isolated in 10–15% yield. The formation of II is analogous to the formation of the substance believed to be 3,4,5,6-tetra-*O*-benzoyl-D-glucose diethyl thioacetal on reaction of D-glucose diethyl thioacetal with benzoyl chloride in aqueous alkali (1). We have found that the tetraacetate (II) behaves in a manner similar to the tetrabenzoate (2) in that it undergoes methylation at the C2-position on treatment with methyl iodide and silver oxide. Deacetylation of the product formed on the methylation of the tetraacetate (II) gave a 56% yield of 2-*O*-methyl-D-glucose diethyl thioacetal (III). The material in the mother liquor was deacetylated and demercaptalated. The only monomethyl derivative of glucose other than 2-*O*-methyl glucose which could be identified in the product by application of the method developed by the authors for identifying mono-*O*-methylglucoses (7) was methyl β-D-glucopyranoside. The formation of the glucoside is attributable to the ability of silver oxide to bring about the demercaptalation of thioacetals (4).

The tetraacetate (II) was found to be identical with the compound prepared by Wolfrom and associates (12) both by detritylation of 6-*O*-trityl-D-glucose diethyl thioacetal tetraacetate (IV) and by mercaptalation of 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranose (V) with ethanethiol containing zinc chloride. Our methylation experiments suggest that compound II is 3,4,5,6-tetra-*O*-acetyl-D-glucose diethyl thioacetal. However, Wolfrom and co-workers have shown (12) that partial demercaptalation of II yields ethyl tetra-*O*-acetyl-α-D-1-thioglucofuranoside (VI). Thus, the free hydroxyl group in II may be at positions 2 or 4. The tetraacetate (II) (and perhaps the tetrabenzoate of Brigl and Mühlschlegel (1)) may undergo preferential methylation at the C2-position for the same reason that D-glucose diethyl thioacetal undergoes preferential methylation at this position (8). Wolfrom and Anno (10) have shown that acetylation of D-glucosamine diethyl thioacetal with acetic anhydride in pyridine has yielded (11) a crystalline tetraacetate. Considering the ease with which amines can be acetylated, this substance, which is closely

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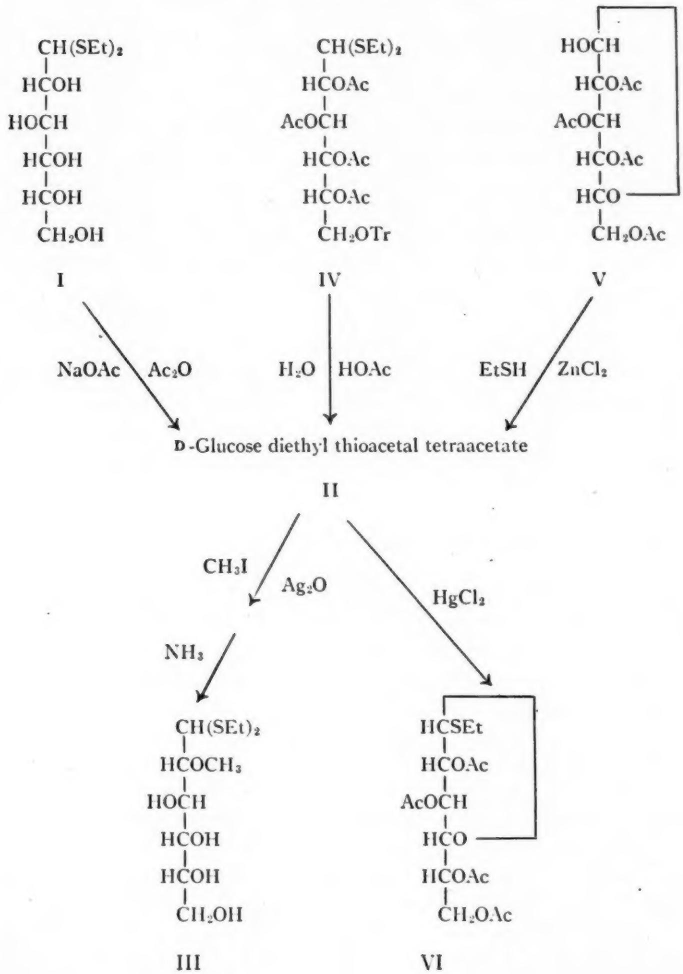

related to the tetraacetate (II) of D-glucose diethyl thioacetal, almost certainly possesses a 2-*N*-acetyl group. It is conceivable that the two tetraacetyl derivatives display resistance to acetylation for the same reason. It is of interest to note that an orthoacid structure could account for the resistance of these compounds toward acetylation. In this respect, it is noteworthy that Doerschuk (3) has confirmed the opinion of Fischer (5) that acyl group migrations are intramolecular and proceed by way of orthoacid intermediates.

In conclusion, the present data show that the tetraacetate (II) is a labile compound which can react as if either position 2 or position 4 were open. The position of the free hydroxyl group remains unknown.

EXPERIMENTAL

The rotations were measured at 22–25°C.

Tetra-O-acetyl-D-glucose Diethyl Thioacetal (II)

A mixture of D-glucose diethyl thioacetal (4), 5 gm., acetic anhydride, 50 ml., and sodium acetate, 5 gm., was heated on the steam bath for 30 min. The solution was stirred with ice water to decompose the anhydride and the mixture was extracted with chloroform. The chloroform solution was washed with aqueous sodium bicarbonate solution and water, dried, and evaporated to a sirup. The sirup readily yielded a crystalline product on being scratched in alcohol. Recrystallization from ethanol gave 1.22 gm. of material, m.p. 117–118°C., $[\alpha]_D$ −23° (*c*, 4 in chloroform), which did not depress the melting point of the tetra-*O*-acetyl-D-glucose diethyl thioacetal of same physical constants prepared by mercaptalation of 2,3,4,6-tetra-*O*-acetyl-β-D-glucose as reported by Wolfrom and co-workers (12). Calc. for $C_{10}H_{18}O_5S_2(CH_3CO)_4$: acetyl, 37.8; S, 14.1%. Found: acetyl, 36.6; S, 13.9%. The substance possessed an absorption band at 3425 cm.$^{-1}$ which is characteristic of hydroxyl groups.

Methylation of the Tetraacetate (II)

The tetraacetate (II), 1 gm., was shaken at room temperature with 5 ml. of dry dioxane, 10 ml. of methyl iodide, 1 gm. of freshly prepared silver oxide, and 1 gm. of Drierite. After two hours, 1 gm. of silver oxide and 0.5 gm. of Drierite were added and the shaking was continued for four hours. The silver salts were collected and washed with methanol. The filtrate was evaporated to a sirup which was dissolved in 30 ml. of saturated methanolic ammonia solution. After standing overnight at 0°C., the solution was evaporated to a crystalline residue which was triturated with ether. Recrystallization from ethanol gave 0.34 gm., 56% yield, of a substance, m.p. 156–157°, $[\alpha]_D$ −25.5° (*c*, 2 in pyridine), which did not depress the melting point of an authentic sample of 2-*O*-methyl-D-glucose diethyl thioacetal (9) of same physical constants.

The mother liquors from the above isolation of 2-*O*-methyl-D-glucose diethyl thioacetal were evaporated to a sirup which was heated for 30 min. on a steam bath with 25 ml. of saturated aqueous mercuric chloride solution in 25 ml. of water. The clarified solution was deionized by using hydrogen sulphide to precipitate the mercuric ions and Amberlite IR4B to remove the hydrochloric acid. Evaporation gave 0.30 gm. of sirup which was found to contain monomethylglucoses as the main component and small amounts of glucose and di-*O*-methylglucoses. The mono-*O*-methylglucose fraction was isolated by preparative paper chromatography (7). The material crystallized after some time. Recrystallization from ethanol gave a substance which was identified as methyl β-D-glucopyranoside by its melting point (110–111°C. with a crystalline transformation at 104–105°C. (6)), specific rotation (−33.1° (*c*,1 in water)), mixed melting point (undepressed) and infrared spectrum (identical to that of the authentic sample). 2-*O*-methyl-D-glucose was the only mono-*O*-methyl-D-glucose which could be identified in the mother liquors by the procedure of Lemieux and Bauer (7).

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THE KINETICS OF THE PYROLYSIS OF ETHYL AND ISOPROPYL FORMATES AND ACETATES[1]

BY ARTHUR T. BLADES

ABSTRACT

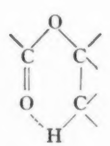
The pyrolysis of ethyl formate, isopropyl formate, ethyl acetate, and isopropyl acetate has been carried out under conditions which favor the decomposition of these esters into the corresponding acid and alkene to the exclusion of side reactions. The rate expressions found were: ethyl formate, $k = 2.13 \times 10^{11}\ e^{-44{,}140 \pm 200/RT}$ sec.$^{-1}$; isopropyl formate, $k = 3.8 \times 10^{12}\ e^{-44{,}000 \pm 100/RT}$ sec.$^{-1}$; ethyl acetate, $k = 3.06 \times 10^{12}\ e^{-47{,}750 \pm 100/RT}$ sec.$^{-1}$; isopropyl acetate, $k = 1.00 \times 10^{13}\ e^{-45{,}000 \pm 100/RT}$ sec^{-1}. The nature of the transition state is discussed and compared with that for similar decompositions.

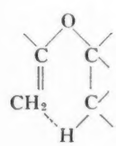
INTRODUCTION

The pyrolysis of esters has been the subject of extensive research (1, 3, 9, 10). In general, for those esters with a β-hydrogen in the alkyl group, the products are the corresponding acid and alkene. Methyl esters are comparatively stable, decomposing only at more elevated temperatures into a variety of products.

Kinetics studies have been made on the decompositions of ethyl (10), isopropyl, and *n*-propyl formates (1), the primary products being the alkene and formic acid. The interpretation of the data was, however, rendered difficult by the decomposition of the formic acid into hydrogen, carbon monoxide, carbon dioxide, water, and formaldehyde.

Hurd and Blunk (9) have proposed a mechanism involving a "cyclic hydrogen bridge" to explain the decomposition of esters into acid and alkene. Recent studies of the decomposition of vinyl alkyl ethers (6, 4) suggest that a similar type of activated complex is involved in the decomposition of these ethers.





The present pyrolyses have been carried out in a flow system with toluene as a carrier gas. Toluene has been used extensively to suppress chain reactions in thermal decompositions where free radicals are produced (11, 6, 7, 4). This research represents a successful attempt to apply this technique to a system in which heterogeneous reactions complicate the normal homogeneous decomposition.

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Contribution from the Department of Chemistry, University of Wisconsin, Madison, Wisconsin, and the National Research Council of Canada, Ottawa, Canada. Issued as N.R.C. No. 3216.
[2] *National Research Laboratories Postdoctorate Fellow 1952–1954.*

EXPERIMENTAL

Similarly designed but different apparatuses were used for the decompositions of the ethyl and isopropyl esters; rate constants for the decomposition of ethyl acetate in the two, however, differed by no more than five per cent and consequently no distinction will be made in their description. Both have been described previously (7, 5).

Briefly, the technique involved the passage of the reactant through a long narrow reaction chamber in the presence of an excess of toluene vapor. The pressure of gas (about 1.5 cm. Hg) was maintained constant and the flow rate regulated by suitable capillaries chosen to give contact times between 0.15 and 0.8 sec. The products were condensed in liquid air traps and the alkenes isolated at the end of the experiment by being pumped off the traps at $-120°$ C. with a Toepler pump. The quantity of acid produced was determined by shaking the liquid products with a few cubic centimeters of water and titrating with 0.1 *N* sodium hydroxide solution. With the formate esters it was necessary to carry out this titration at 5° C. to prevent the hydrolysis of the undecomposed ester.

The esters (Eastman) were purified by distillation on an efficient column.

Ethyl formate, b.p. 52.1° C. at 728 mm.

Isopropyl formate, b.p. 69.0° C. at 768 mm.

Ethyl acetate, b.p. 76.8° C. at 748 mm.

Isopropyl acetate, b.p. 88.7° C. at 764 mm.

RESULTS

The only products found in all of these pyrolyses were the corresponding acids and alkenes. No appreciable quantity of any of the normal decomposition products of the acids was detected even at the highest temperatures, i.e. 650° C. nor was there any evidence of the production of bibenzyl as would have been expected if the reaction had involved the production of free radicals.

The equivalence of acid and alkene was demonstrated in the products of the decomposition of each compound. By varying the flow rate of the gases in the reactor it was demonstrated that the rate of production of acid obeyed a first order rate expression up to 70 to 80% decomposition of these esters (see Table I, Expts. 6, 7, 8; 9, 10, 11; Table II, Expts. 8, 9, 10; 11, 12, 13, 14; Table III, Expts. 6, 7, 8; Table IV, Expts. 9, 10, 11; 14, 15, 16).

Fitting the data in Tables I, II, III, and IV to the Arrhenius equation by the method of least squares yields the following rate expressions.

Ethyl formate, $k = 2.13 \times 10^{11}\, e^{-44,140 \pm 200/RT}$ sec^{-1}.

Isopropyl formate, $k = 3.8 \times 10^{12}\, e^{-44,000 \pm 100/RT}$ sec^{-1}.

Ethyl acetate, $k = 3.06 \times 10^{12}\, e^{-47,750 \pm 100/RT}$ sec^{-1}.

Isopropyl acetate, $k = 1.00 \times 10^{13}\, e^{-45,000 \pm 100/RT}$ sec^{-1}.

Plots of these data are shown in Figs. 1 and 2.

By comparing these rate expressions with the absolute rate theory equation

$$k = \kappa \frac{k'T}{h} e^{\Delta S^{\ddagger}/R} e^{-\Delta H/RT} \text{ sec.}^{-1}$$

TABLE I
RATE STUDIES ON ETHYL FORMATE

Expt. Number	Total moles	Pressure, cm. Hg	Contact time, sec.	% Decomp.	Temp., ° K.	k, sec.$^{-1}$
1	.0453	2.07	.710	17.1	810.6	0.264
2	.0451	2.06	.693	30.3	831.2	0.521
3	.0450	2.07	.685	43.3	845.4	0.827
4	.0770	1.47	.281	29.7	857.5	1.25
5	.0534	1.84	.504	52.3	864.0	1.47
6	.0869	1.66	.278	40.0	869.7	1.84
7	.0566	1.96	.503	58.6	869.8	1.75
8	.0452	2.11	.675	68.1	869.7	1.68
9	.0581	1.50	.278	48.2	880.1	2.36
10	.0431	2.03	.675	79.6	880.0	2.34
11	.0545	1.90	.499	68.6	880.0	2.31
12	.0535	1.85	.491	73.2	886.7	2.68
13	.0809	1.54	.261	83.7	920.0	6.92

TABLE II
RATE STUDIES ON ISOPROPYL FORMATE

Expt. Number	Total moles	Pressure, cm. Hg	Contact time, sec.	% Decomp.	Temp., ° K.	k, sec.$^{-1}$
1	.0477	2.12	.813	14.3	721.3	0.189
2	.0563	2.15	.692	17.4	732.0	0.276
3	.0753	1.92	.459	12.5	733.0	0.290
4	.0590	1.82	.459	17.5	742.2	0.417
5	.0841	1.84	.384	21.3	752.4	0.622
6	.0832	1.82	.380	31.5	764.0	1.00
7	.0894	1.69	.375	44.9	776.4	1.59
8	.0804	1.75	.366	56.2	786.2	2.25
9	.0808	1.75	.364	57.3	786.8	2.34
10	.0706	1.83	.436	63.8	787.0	2.33
11	.0953	1.43	.248	59.8	800.0	3.66
12	.0774	1.71	.364	74.0	800.1	3.68
13	.1163	1.06	.150	42.4	800.2	3.68
14	.0665	1.76	.437	79.8	800.3	3.63
15	.0941	1.44	.250	74.5	810.6	5.44

TABLE III
RATE STUDIES ON ETHYL ACETATE

Expt. Number	Total moles	Pressure, cm. Hg	Contact time, sec.	% Decomp.	Temp., ° K.	k, sec.$^{-1}$
1	.0475	1.88	.792	12.5	787.2	0.169
2	.0381	1.86	.767	20.5	802.0	0.299
3	.0499	1.63	.505	22.8	816.9	0.514
4	.0498	1.63	.502	27.6	822.8	0.642
5	.0505	1.65	.490	42.4	839.0	1.12
6	.0697	1.28	.286	36.0	848.3	1.56
7	.0385	1.91	.736	67.5	848.0	1.52
8	.0521	1.63	.489	52.5	848.5	1.51
9	.0606	1.19	.286	53.1	864.8	2.64
10	.0632	1.24	.280	73.0	883.4	4.67

TABLE IV
RATE STUDIES ON ISOPROPYL ACETATE

Expt. Number	Total moles	Pressure, cm. Hg	Contact time, sec.	% Decomp.	Temp., ° K.	*k*, sec.$^{-1}$
1	.0690	2.28	.814	12.5	714.7	0.163
2	.0561	2.22	.808	16.6	722.2	0.225
3	.0519	2.27	.795	21.0	728.6	0.297
4	.0899	1.95	.459	12.7	729.3	0.296
5	.0773	1.97	.457	21.0	739.7	0.514
6	.0753	1.92	.457	19.6	739.7	0.477
7	.0755	1.92	.444	34.2	757.0	0.943
8	.0773	1.97	.441	45.4	766.5	1.37
9	.0678	1.78	.448	59.0	775.8	1.98
10	.0506	2.05	.677	74.0	775.8	1.99
11	.0978	1.47	.257	40.2	776.0	2.00
12	.1043	1.55	.249	52.7	787.8	3.01
13	.1001	1.45	.257	55.4	788.3	3.15
14	.1123	1.03	.152	52.6	800.7	4.92
15	.1147	1.05	.152	53.3	801.0	5.01
16	.0973	1.47	.250	70.9	801.0	4.95

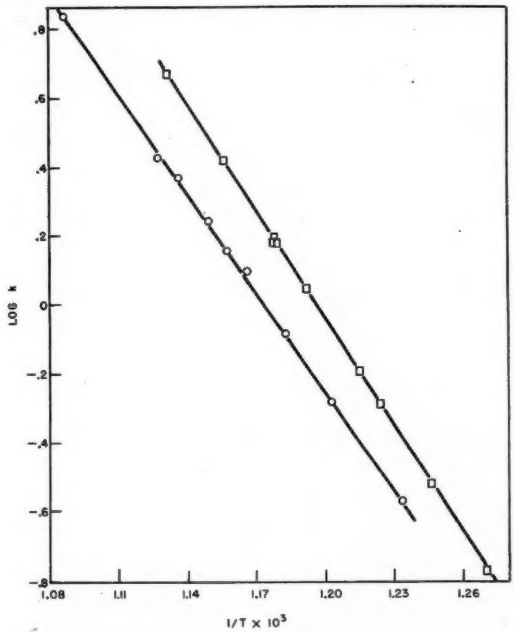

FIG. 1. The temperature coefficient of the rate.
○ Ethyl formate. □ Ethyl acetate.

and assuming that the transmission coefficient κ is unity, the following entropies of activation are obtained.

Ethyl formate $\Delta S^{\ddagger} = -10.7$ e.u. at 800° K.
Isopropyl formate $\Delta S^{\ddagger} = -4.9$ e.u. at 800° K.

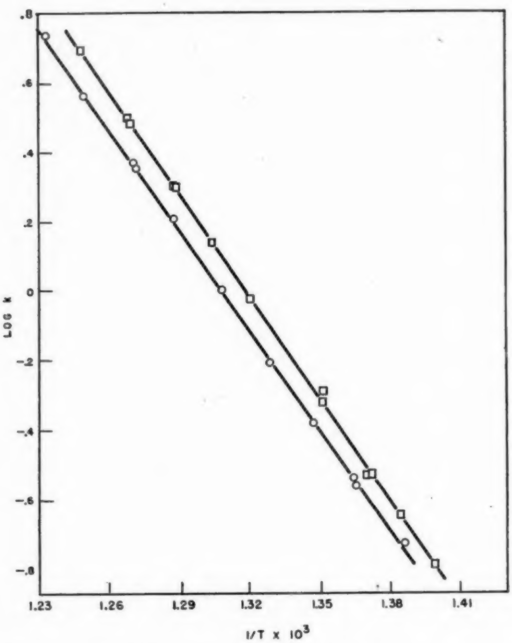

FIG. 2. The temperature coefficient of the rate.
○ Isopropyl formate. □ Isopropyl acetate.

Ethyl acetate	$\Delta S^{\ddagger}$	=	-5.4 e.u. at 800° K.
Isopropyl acetate	$\Delta S^{\ddagger}$	=	-3.0 e.u. at 800° K.

DISCUSSION

The molecular nature of the mechanism for the decomposition of esters with a β-hydrogen in the alkyl group is confirmed by the present research. If free radicals were produced they would be expected to react with the excess of toluene.

$$R^{\cdot} + C_6H_5CH_3 \rightarrow RH + C_6H_5\dot{C}H_2$$

The benzyl radicals would dimerize to bibenzyl. The lack of bibenzyl among the products is then good evidence against any free radical mechanism.

That the presence of the toluene prevented the normally heterogeneous decomposition of both the acids and esters suggests that these decompositions are free radical chain reactions initiated at the wall. Hinshelwood (8) has shown that the decomposition of methyl formate is sensitized by the photolysis of acetaldehyde, indicating that esters are, indeed, susceptible to radical chain decomposition.

The rate expression previously reported for the decomposition of ethyl formate (10) ($k = 2.52 \times 10^9\ e^{-40,010/RT}$ sec.$^{-1}$) compares unfavorably with that found in the present research. Rates calculated from the two expressions

are sufficiently similar, however, to conclude that the same reaction is involved. For isopropyl formate, the rate expression found by Anderson and Rowley (1) ($k = 2.47 \times 10^{12}\, e^{-44,230/RT}$ sec.$^{-1}$) is very close to that recorded here.

The activation energies found for ethyl formate (44,140 cal./mole) and isopropyl formate (44,000 cal./mole) are identical within the experimental error. In this regard, these esters behave like ethyl vinyl ether (43,800 cal./mole) and isopropyl vinyl ether (43,560 cal./mole). The activation energies for the corresponding acetates (i.e. 47,750 and 45,000 cal./mole) are slightly higher and differ by considerably more than the experimental error. The difference between the activation energies for the formates and acetates is probably due to hyperconjugation in the normal acetate molecule which is absent in the transition state. No explanation can be given to account for the difference in activation energy between the ethyl and isopropyl acetates.

An interesting feature of this series of compounds is the negative value of the entropy of activation. Such a value is consistent with the formation of the cyclic transition state suggested by Hurd and Blunk (9) since three internal rotational degrees of freedom are converted to relatively inactive vibrations in the process of activation.

The regular trend in the entropy of activation as successive methyl groups are added to the molecule is predictable on the basis of the increased number of β-hydrogen atoms available for the formation of the activated complex, and of the increased restriction of internal rotation in the normal molecule. The effect of the increased moment of inertia, which would have the opposite effect, seems to be very small compared to the other two.

Remarkably similar entropies of activation were also observed in the decomposition of ethyl vinyl ether (6) ($\Delta S^{\ddagger} = -10.2$ e.u. at 800° K.) and isopropyl vinyl ether (4) ($\Delta S^{\ddagger} = -4.8$ e.u. at 760° K.), which differ from the ethyl and isopropyl formates only in the substitution of a methylene group for an oxygen atom. This similarity lends considerable support to the belief that similar activated complexes are involved in the decomposition of esters and vinyl ethers.

Finally, it is worthy of note that in this series of compounds which decompose via similar mechanisms, there is no suggestion of any relation between the logarithm of the frequency factor and the activation energy as has been found by Barton *et al.* (2) in the decomposition of alkyl chlorides. In fact, there is evidence for complete independence of the two variables.

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STUDIES IN THE POLYOXYPHENOL SERIES

VI. THE OXIDATION OF PYROGALLOL AND VANILLIN BY ALKALINE HYPOIODITE AND HYPOCHLORITE[1]

By G. Denis Thorn[2] and C. B. Purves

ABSTRACT

Approximately 0.003 M solutions of pyrogallol and of vanillin in boric acid – sodium hydroxide buffers were used at 25°C. to reduce hypoiodite and hypochlorite solutions made from sixfold molar amounts of the halogens. In all four cases the reduction reached a maximum in a narrow range near pH 9, and with hypoiodite the production of iodoform was restricted to this range. Slower secondary reductions were superimposed on very fast primary reactions. When oxidized with an equimolecular amount of halogen near pH 8.5, vanillin gave a 90% yield of 5-iodovanillin and 65% of the 5-chloro derivative. These yields decreased with increasing alkalinity as the halogenations became slower. A new, simple preparation of trichloropyrogallol in 72% yield consisted of carrying out the chlorination with 3 moles of hypochlorite at pH 12. An equilibrium between pyrogallol–hypoiodite and 3-hydroxy-1,2-benzoquinone–iodide appeared to exist at the same pH.

INTRODUCTION

Numerous researches have shown that a proper control of the hydrogen ion concentration and similar variables is of great importance in the removal of residual lignin from wood pulps by bleaching with alkaline hypochlorite. The results are difficult to interpret in a chemical sense because little is known about the structure of lignin beyond the fact that it is in great part based upon phenolic units related to vanillin and syringaldehyde. Soper and Smith (26), however, showed that simple monohydric phenols reacted with hypochlorous acid at a rate directly proportional to the concentration of the hydroxyl ion in the region of pH 7, but that the rate became inversely proportional near pH 12. Hypochlorous acid, unlike free chlorine, had no action on phenolic ethers, and the oxidation of phenols by hypoiodite was relatively slow. The last observation had its counterpart in the lignin field, because Hixon and his collaborators (5, 29) found that the consumption of alkaline hypoiodite by various lignins ceased at a rather low limit, whereas the consumption of hypochlorite proceeded almost indefinitely. The present research had the object of gaining information about the conditions necessary for the "limited" action of excess hypoiodite on simple phenols, and of discovering whether the action of hypochlorite could also be limited. Pyrogallol and vanillin were chosen for the study because the results might eventually prove relevant to lignin.

REACTIONS WITH ALKALINE HYPOIODITE

The initial experiments were carried out with dilute aqueous solutions of pyrogallol containing a sixfold molar amount of iodine, and buffered with

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Contribution from the Division of Industrial and Cellulose Chemistry, McGill University, and the Wood Chemistry Division, Pulp and Paper Research Institute of Canada, Montreal, Que. Abstracted from a Ph.D. Thesis submitted by G. D. T. in September, 1947.
[2] *Holder of a National Research Council of Canada Studentship in 1945-6, and of a Fellowship in 1946-7. Present address: Science Service Laboratory, Department of Agriculture, London, Ont.*

boric acid – sodium hydroxide (Table I). Since hypoiodite rapidly decomposed to iodate and iodide in solutions containing excess alkali (23), the estimation of unused hypoiodite at any time had to include the by-product iodate. This

TABLE I

REDUCTION OF HYPOIODITE BY PYROGALLOL DURING 24 HR. AT 25°C.[a]

Run	NaOH M	pH	Moles HIO reduced[b]	Run	NaOH M	pH	Moles HIO reduced[b]
Boric acid, 0.2 M; I_2, 0.0204 M				Unbuffered; I_2, 0.21 M			
1	0.04	8.0[c]	4.8	19	0.54	12.5	2.8
2	0.10	8.6	4.9	20	0.61	13	2.7
3	0.16	9.4	5.3	21	0.63	>13	2.65
4	0.21	9.7	4.1	Unbuffered; I_2, 0.0205 M			
5	0.26	12.0	1.25	22	0.05	11.7	2.4
6	0.31	12.5	1.7	Boric acid, 0.2M; I_2, 0.0205 M			
7	0.36	>13	1.7	23	0.26	11.9	0.71
8	0.42	>13	1.7	24[d]	0.26	11.9	0.74
9	0.47	>13	2.5	25[e]	0.26	11.9	0.72

[a] *All concentrations in moles per liter, the molar ratio of iodine to pyrogallol being 6 : 1.*
[b] *Per mole of pyrogallol.*
[c] *Final pH was 6.7 after 17.5 hr.*
[d] *Molar ratio of iodine to pyrogallol, 3 : 1.*
[e] *Molar ratio of iodine to pyrogallol, 2 : 1.*

objective was attained by titrating the iodine liberated when aliquots were strongly acidified, and control experiments showed that the iodine consumed after the acidification was probably not more than 0.15 mole per mole of pyrogallol.

Columns 4 and 8 of Table I record the molar amounts of iodine (or hypoiodite) reduced by 1 mole of pyrogallol after 24 hr., when the reaction had certainly ceased. These amounts passed through a maximum of 5.3 moles near pH 9.4 (run 3), and through a minimum of 1.25 moles near pH 12 (runs 5 to 9). Omission of the borate buffer and a 10-fold increase in the concentration both of iodine and pyrogallol gave solutions whose pH decreased seriously during the reaction unless the molarity of sodium hydroxide was at least 0.54 (run 19), but a greater concentration of alkali had little effect (runs 20, 21). Although the minimum of 1.25 moles near pH 12 was not maintained in the absence of the buffer (run 22), buffered solutions retained the minimum even when the molar ratio of iodine to pyrogallol was reduced from 6 : 1 to 3 : 1 and 2 : 1 (runs 23 to 25). The titrations in these particular runs could not be closely reproduced, and consumptions of iodine as high as 0.87 moles were observed at intermediate times.

The initial portions of the rate-plots for runs 1 to 6, and also for runs 9 and 25, (Fig. 1) clearly showed that the first stage in the reaction was always very

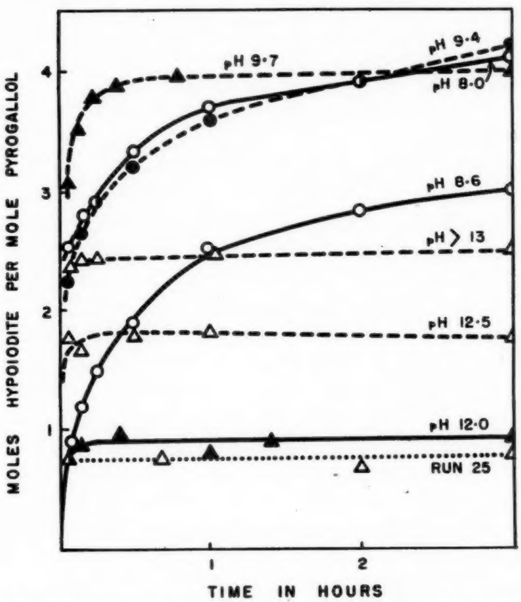
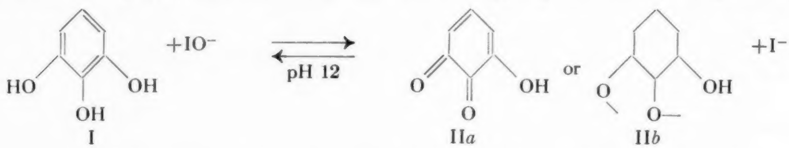


FIG. 1. Initial rate of reaction of 0.0033 *M* pyrogallol with 0.02 *M* iodine at 25°C. Moles of iodine reduced per mole of pyrogallol at the pH values shown. Run 25 with 0.01 *M* pyrogallol.

rapid, and that the ultimate consumption of iodine by the pyrogallol (Table I) depended on the progress of secondary reactions. These secondary reactions were most extensive at pH 9.4 and decreased to zero, both in speed and in amount, near pH 12. The minimum at the latter pH was not caused by the prior conversion of all excess hypoiodite to iodate, because the consumption was about 2.5 times greater in stronger alkali (pH > 13) where competition with the conversion to iodate would be still more serious (23). The first four oxidations (Table I) resulted in pale orange solutions, of which the first and fourth deposited only traces of iodoform, whereas the second and third yielded 0.14 and 0.16 moles respectively, per mole of pyrogallol. Iodoform was therefore produced only in the range pH 8.6 to 9.4, when the secondary reaction was unusually extensive and prolonged.

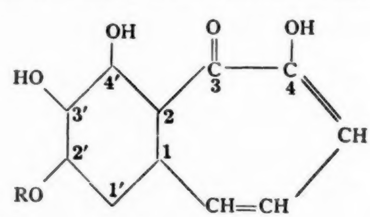
Since about one mole of iodine was reduced by pyrogallol (Structure I) at pH 12, the initial product could not be of a complicated nature, and the dark red color of the solution indicated the presence of a quinonoid rather than an aromatic structure. The most probable assumption (25, 33) for the initial product was the very labile 3-hydroxy-1,2-benzoquinone, (II*a*), or the corresponding radical (II*b*), (10) or other tautomer. Subsequent oxidations were carried out with equimolar amounts of iodine and pyrogallol in a borate

buffer at pH 12, and, as the solutions were reproducible and stable for hours, they were designated "oxidized pyrogallol solutions." In accord with the above assumption, the red color of the "oxidized pyrogallol solution" lightened



considerably when zinc dust was added as a reducing agent, and subsequent acetylation of the alkaline solution with acetic anhydride (3) recovered at least 52% of the pyrogallol as the crystalline triacetate. Sodium hydrosulphite also discharged the color of the solution to a light yellow, but pyrogallol triacetate could not be recovered, perhaps because sulphonation occurred (11). Although the addition of sodium thiosulphate failed to reduce the color of the solution noticeably, and presumably failed to reduce the supposed quinone, the subsequent acetylation gave an 89% yield of pyrogallol triacetate. The "oxidized pyrogallol solution" was then acetylated without prior reduction, and a control acetylation was made with a solution from which the iodine had been omitted. Pyrogallol triacetate was isolated in yields of 89% and 87%, respectively, from the two experiments. These observations suggested that the "oxidized pyrogallol solution" contained pyrogallol and hypoiodite in equilibrium with the hydroxyquinone and iodide, and that acetylation of the pyrogallol drove the equilibrium far to the left with the regeneration of hypoiodite. Aliquots of the solution, when acidified and titrated with standard sodium thiosulphate immediately before and after the acetylation, were found to contain 41% and 92%, respectively, of the original hypoiodite. An application of the law of mass action showed that the former figure corresponded to consumptions of 0.83 and 0.97 moles of iodine per mole of pyrogallol when the iodine was in twofold and sixfold molar amounts. The values found were of the same order (Fig. 1, run 25 and plot pH 12).

An attempt was then made to isolate the supposed 3-hydroxy-1,2-benzoquinone by acidifying the "oxidized pyrogallol solution" and extracting it with ether. Acidification with sulphuric acid, however, caused the prompt deposition of crystalline purpurogallin in 25% of the theoretical yield. Haworth and his collaborators (18) recently showed that purpurogallin had the structure (III, R = H). The ether extract from solutions acidified with acetic acid



III (R = H or CH_3)

contained dark red substances from which 17% to 46% yields of orange-red crystals were obtained after acetylation with an acidic catalyst. These crystals, melting at 162° to 163°C. were later identified (28) as a new triacetate of purpurogallin. In an endeavor to avoid the use of acid, the "oxidized pyrogallol solution" was methylated with dimethyl sulphate on the alkaline side of pH 10, and extraction of the methylated liquors with ethyl acetate recovered about 35% of the pyrogallol as an orange residue. The residue yielded the dark red needles of 2′-monomethyl purpurogallin (III; $R = CH_3$), which had been obtained by oxidizing a mixture of pyrogallol and its 1-methyl ether with hydrogen peroxide and peroxidase (33), or with potassium iodate (7). Since the production of purpurogallin from pyrogallol almost certainly required 3-hydroxy-1,2-benzoquinone (II) as an intermediate (6, 7, 33), the results supported the view that the quinone (or a tautomer) was present as such in the "oxidized pyrogallol solution". The experiments, however, failed to circumvent the great tendency of *o*-quinones to condense when in acid solution (12, 24, 27), and even the temporary local acidity accompanying the methylation apparently promoted condensation.

The oxidation of vanillin by a sixfold molar amount of iodine in sodium borate buffers, when continued to completion (Table II) revealed a maximum consumption of about 3.65 moles per mole near pH 10 (run 4). This maximum corresponded to a particularly rapid secondary oxidation during the first three hours, as shown in Fig. 2, in which the plots for the intermediate runs 2, 5, and 10 were not reproduced. Small, red, flocculent precipitates were

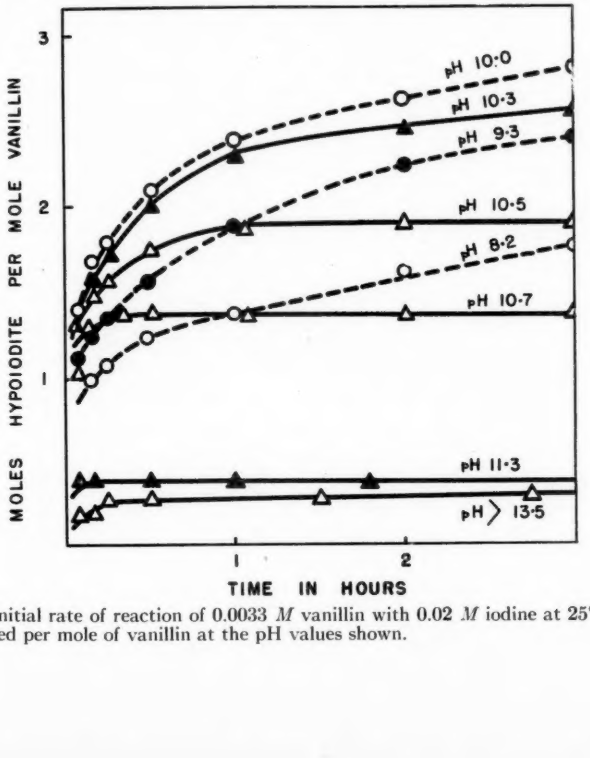


FIG. 2. Initial rate of reaction of 0.0033 *M* vanillin with 0.02 *M* iodine at 25°C. Moles of iodine reduced per mole of vanillin at the pH values shown.

formed in runs 1 to 5 (pH 8.2 to 10.2), and the mother liquors from these runs yielded 0.15, 0.16, 0.12, 0.06, and 0.0 moles of iodoform per mole of vanillin. As in the case of pyrogallol, therefore, the production of iodoform was at a maximum near pH 9, or when the secondary oxidation was approaching its greatest extent. Since vanillin very rapidly consumed about one mole of iodine in the pH range 8.2 to 10.7, equimolar amounts of vanillin and iodine were used in order to isolate the product of the initial reaction. Crystalline 5-iodovanillin was recovered in 90% yield from the reaction at pH 8.2, whereas the yield at pH 10 was only 62%, and 31% of hypoiodite remained at the end of the arbitrary period of 15 min. Although the oxidations at pH 11 or greater were not examined in detail, the lack of color in the solutions suggested the absence of quinones, and the small consumption of iodine put an upper limit of 35% on the production of 5-iodovanillin. The halogenating action of iodine on vanillin thus decreased abruptly on the alkaline side of pH 10. Erdtman's (9) similar preparation gave 73% of recrystallized 5-iodovanillin, and must therefore have been made in, or close to, the optimum pH range.

TABLE II
REDUCTION OF HYPOIODITE BY VANILLIN DURING 24 HR. AT 25°C.[a]

Run	NaOH *M*	pH	Moles HIO reduced[b]	Run	NaOH *M*	pH	Moles HIO reduced[b]
1	0.04	8.2	2.7	7	0.22	10.5	1.9
2	0.06	8.9	2.75	8	0.23	10.7	1.35
3	0.10	9.3	3.3	9	0.24	11.3	0.35[c]
4	0.16	10.0	3.65	10	0.28	12.6	0.3
5	0.20	10.2	3.2	11	0.32	13.5	0.3
6	0.21	10.3	2.6				

[a]*In 0.2 M boric acid, 0.02 molar in iodine and 0.0033 molar in vanillin (mole ratio 6 : 1).*
[b]*Per mole of vanillin.*
[c]*Constant from 1 hr. to 9 hr.*

REACTIONS WITH ALKALINE HYPOCHLORITE

The oxidation of pyrogallol with six times the molar amount of sodium hypochlorite in adequate borate buffers proceeded at all the pH values studied until the oxidant was almost entirely exhausted. Table III records the consumptions of oxidant after nine hours, when the oxidation at pH 8.8 (run 2) was practically complete; thereafter the necessary time increased to more than 24 hr. at pH 12.4 (run 8). The initial portions of the rate plots for runs 1, 3, 4, 5, 7, and 8 (Fig. 3) revealed a very rapid consumption of about three moles of hypochlorite per mole of pyrogallol, and a secondary consumption whose rate and extent went through a maximum near pH 11. These observations were supported by the plots at intermediate pH values (runs 2 and 6, not reproduced). The solutions remained colorless in the first three experiments (pH 8 to 9) but in the others initially ranged from light yellow to orange, becoming colorless only after 15 to 30 min. No precipitate was observed in any of the runs.

Pyrogallol, when mixed with a 3-molar proportion of chlorine dissolved in 10% sodium carbonate solution, within 10 min. gave a 72% yield of crystalline

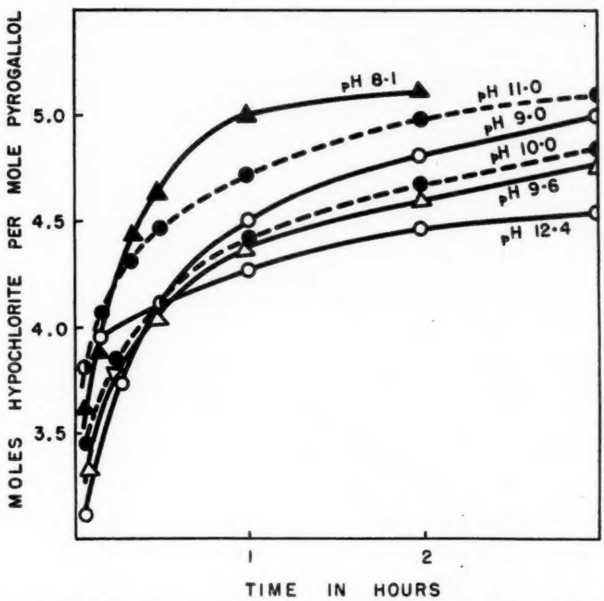


FIG. 3. Initial rate of reaction of 0.003 *M* to 0.004 *M* pyrogallol with a sixfold molar concentration of chlorine at 25°C. Moles of chlorine reduced per mole of pyrogallol at the pH values shown. Plot at pH 8.1 with 5.13 molar equivalents of chlorine.

trichloropyrogallol monohydrate. Even near pH 12, therefore, the initial action of hypochlorite was one of halogenation, and constituted a new and convenient method of preparing the trichloro derivative in good yield. The product was always contaminated with boric acid when a borate buffer was used in the preparation, and attempts to isolate the triacetate by adding acetic anhydride to the alkaline solution (3) failed. Webster (30) obtained

TABLE III

REDUCTION OF HYPOCHLORITE BY PYROGALLOL DURING NINE HOURS AT 25°C.[a]

Run	NaOH M	Cl_2 $M \times 10^2$	Pyrogallol $M \times 10^2$	pH	Moles HClO reduced[b]
1	0 03	1.54	0.299	8.1	5.1[c]
2	0.10	1.96	0.327	8.8	5.9
3	0.12	1.96	0.327	9.0	5.6
4	0.16	1.96	0.327	9.6	5.3
5	0.20	1.96	0.327	10.0	5.3
6	0.22	1.96	0.327	10.5	5.4
7	0.24	2.4	0.40	11.0	5.5[d]
8	0.28	2.4	0.40	12.4	5.0[e]

[a]*In 0.2 M boric acid with chlorine to pyrogallol in molar ratio 6 : 1.*
[b]*Per mole of pyrogallol.*
[c]*Chlorine to pyrogallol molar ratio 5.13 to 1. Oxidant exhausted after two hours.*
[d]*After nine hours pH was 10.6; after 24 hr. consumption was 5.94 moles.*
[e]*Consumption 5.4 moles after 24 hr.*

trichloropyrogallol in unstated yield by chlorinating pyrogallol in acetic acid, and Biétrix (1) in poor yield by chlorinating gallic acid suspended in chloroform. Biétrix also prepared the crystalline trichloro-triacetate.

The reduction of hypochlorite by vanillin was examined as in the case of pyrogallol and the details were therefore omitted from the experimental portion of this article. Vanillin consumed all of the oxidant much more rapidly than pyrogallol, but the minimum time required for complete reaction was at a pH near 10 (Table IV, run 5). The initial portions of the rate plots for runs 1, 3, 5, 7, and 8, together with the plots of the intermediate runs not shown in Fig. 4, showed, as expected, that the extent of the secondary reduction was

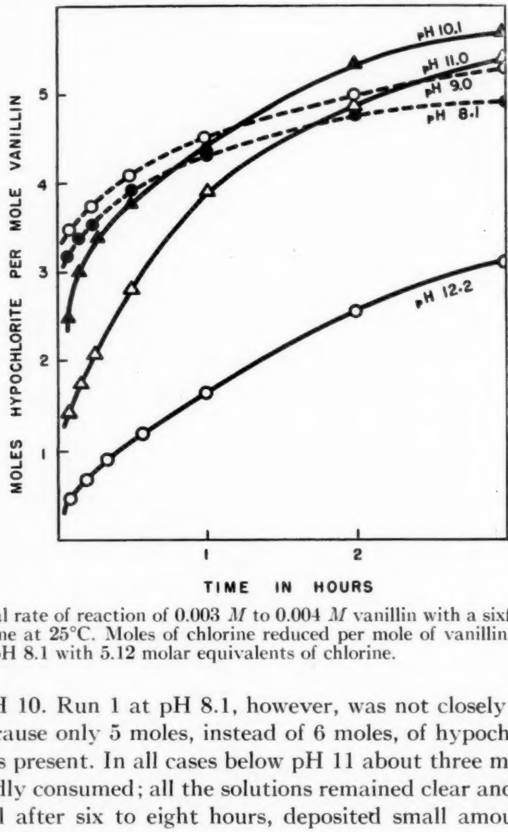


FIG. 4. Initial rate of reaction of 0.003 M to 0.004 M vanillin with a sixfold molar concentration of chlorine at 25°C. Moles of chlorine reduced per mole of vanillin at the pH values shown. Plot at pH 8.1 with 5.12 molar equivalents of chlorine.

greatest at pH 10. Run 1 at pH 8.1, however, was not closely comparable to the others because only 5 moles, instead of 6 moles, of hypochlorite per mole of vanillin was present. In all cases below pH 11 about three moles of chlorine was very rapidly consumed; all the solutions remained clear and colorless, but, when acidified after six to eight hours, deposited small amounts of a pink, flocculent substance.

Runs 2 and 8 (pH 8.7 and 12.2), when repeated with equimolecular amounts of vanillin and chlorine, required 10 min. and 60 min. respectively, for the oxidant to disappear. A 65% yield of 5-chlorovanillin resulted from the former experiment, but the latter gave only 43%, and 38% of the vanillin was recovered as the crystalline 2,4-dinitrophenylhydrazone. Since these figures

failed to account for about 19% of the vanillin and 57% of the chlorine, another reaction probably occurred involving the two components in the 1 : 3 molar ratio. These observations, together with a consideration of Fig. 4, showed that the initial reaction, consuming 3 moles of chlorine almost instantly at lower pH values, became quite slow at pH 12.2, although its nature probably did not change. Hopkins and Chisholm (20) obtained a 90% yield of 5-chlorovanillin by permitting 1.5 moles of sodium hypochlorite to act on 1 mole of vanillin for one hour, apparently in a sodium carbonate buffer.

TABLE IV
REDUCTION OF HYPOCHLORITE BY VANILLIN AT 25°C.[a]

Run	NaOH M	Cl_2 $M \times 10^2$	Vanillin $M \times 10^2$	pH	Hours[b]
1	0.08	1.54	0.30	8.1	2.6[c]
2	0.10	2.4	0.40	8.7	5
3	0.12	2.4	0.40	9.0	5
4	0.16	2.4	0.40	9.5	5
5	0.20	2.3	0.38	10.1	3
6	0.22	2.3	0.38	10.5	4
7	0.24	2.3	0.38	11.0	5
8	0.28	2.3	0.38	12.2	9[d]

[a]*In 0.2 M boric acid with chlorine to vanillin in molar ratio 6 : 1.*
[b]*Approximate time when 93% to 95% of the hydrochlorite was reduced.*
[c]*Chlorine-vanillin molar ratio 5.1 : 1.*
[d]*Only 4.7 moles (52%) of chlorine reduced in nine hours.*

DISCUSSION

Since the reduction of hypoiodite by pyrogallol ranged from about one mole to 5.3 moles, and of vanillin from 1.9 mole to 3.65 moles, according to the hydrogen ion concentration (Tables I and II), this factor required very close control when phenols were estimated by iodometric methods. Failure to observe this requirement in the same way or to the same extent explained why Messinger and Vortman (21) found that 1 mole of various phenols reduced integral even numbers of iodine atoms, and why Orloff (22) thought that the molar consumption in 24 hr. to 48 hr. was fractional. Orloff decided that pyrogallol required approximately five moles, but later workers (15, 25) varied the technique of the estimation and claimed that exactly 3 moles was reduced in a short time. This figure was again revised to approximately five moles (4). Wilkie (31, 32) carefully compared several of the older methods.

As already mentioned, iodoform was produced both from pyrogallol and from vanillin only in a narrow range about pH 9. Booth and Saunders (2) presumably operated in this range when they obtained iodoform by adding sodium hydroxide to a solution of pyrogallol and iodine, but none was observed by Slotta and Neisser (25), who added iodine to a solution of pyrogallol in aqueous sodium carbonate (pH $\sim$ 12). Since iodoform could also be derived on occasion from various *o*- and *p*-hydroquinones (2, 25), from gallic acid, resorcinol, and phloroglucinol (2), the standard iodoform test for the

$CH_3CO—C\equiv$ and related groupings (13, 14) became ambiguous when phenols were present. The production of iodoform (or chloroform) from lignins oxidized by alkaline hypohalites (17, 29) was therefore no decisive proof that lignin contained either methyl ketone or $CH_3CH(OH)—C\equiv$ units.

Green (16), who reviewed the inorganic chemistry of the hypohalites, quoted the dissociation constant of dilute aqueous hypochlorous acid as 6.5×10^{-8}, and of hypoiodous acid as of the order 5×10^{-13}. The former acid was therefore 79% dissociated to the hypochlorite ion at pH 8, and to practically 100% at pH 12; whereas the figures for the latter acid were about 0.005% and 49.5%, respectively. The species of oxidant present in alkaline solutions of iodine therefore varied greatly with pH, but change in the hypochlorite system was minor. With hypochlorite, the halogenating took precedence over the oxidizing action both for pyrogallol and for vanillin even at pH 12, when halogenation by hypoiodite was absent or slow.

If the standard potential of the redox system $H_2O + Cl^- = HClO + H^+ + 2e^-$ in acid solution was accepted as $E_0 = -1.49$ volts, and that of the corresponding iodide–hypoiodite couple as $E_0 = -0.99$ v. (16), calculation showed that these values corresponded to effective oxidation potentials of -1.14 v. and -0.64 v., respectively, at pH 12. When allowance was made for the approximate nature of the calculation, at pH 12 even hypochlorite might not oxidize vanillin, whose "critical oxidation potential" of $E_c = -1.08$ v. was among the highest found by Fieser (10) for the numerous phenols he examined. Since the "critical oxidation potential" of pyrogallol was $E_c = -0.609$ v., and the calculated normal potential of 3-hydroxy-1,2-benzoquinone was $E = 0.677$ v., the promotion of an equilibrium between these substances by hypoiodite at pH 12 might have been anticipated. These physical considerations supported the view that the action of the hypohalites on phenols became "limited", or less complex, on the alkaline side of pH 11 or 12.

EXPERIMENTAL

Rate of Oxidation of Pyrogallol with Hypoiodite (Table I, Fig. 1)

In a typical experiment, 150 cc. of 0.667 *M* aqueous boric acid and the desired volume of 1.0 *N* sodium hydroxide were mixed in a 500 cc. volumetric flask; the mixture was diluted to about 250 cc. with distilled water, and 200 cc. of 0.1 *N* iodine (0.02 equivalents) in aqueous potassium iodide was added. The pH of the solution was measured with a Coleman Model 3 pH Electrometer, with correction as described by Dole (8) for the salt error of the glass electrode. Control experiments with a high alkalinity glass electrode showed that this correction was valid. At zero time, a solution of about 0.21 gm. of pyrogallol (about 0.0017 mole or one-sixth the molar amount of iodine) in 25 cc. of water was added; the total volume was made up to 500 cc. with distilled water, and was promptly and thoroughly mixed. The iodine and pyrogallol solutions had been brought to 25°C. prior to mixing, and were subsequently maintained at 25° ± 0.05°C. in a constant temperature bath. The

pH of the solution was measured at intervals, and runs in which the value decreased by more than 0.3 units in 24 hr. were rejected.

After various times, 10 cc. aliquots were discharged into a large excess, 100 cc., of 1% sulphuric acid, and the iodine liberated was promptly titrated with 0.025 *N* sodium thiosulphate. The starch indicator used was added before the titration was begun, since approach to the end point was masked by the color of the solution. It was necessary to accept the first end point reached, since traces of iodine continued to be liberated for some time in the acid solution.

To assess the error caused by acidifying the solution for titration, 0.047 millimoles of pyrogallol (5.78 mgm.) was added to 50 cc. of 2% sulphuric acid mixed with 50 cc. of 0.006 *N* iodine in potassium iodide. A prompt back-titration with 0.023 *N* sodium thiosulphate required 11.83 cc., when the first end point was accepted, whereas the value for a blank containing no pyrogallol was 12.30 cc. These data corresponded to a consumption of 0.12 mole of iodine per mole of pyrogallol; similar estimations with a 4 : 1 instead of a 6 : 1 molar ratio of iodine to pyrogallol were 0.11 and 0.14 moles.

Oxidations carried out at pH 8.6 and 9.4 (runs 2 and 3) deposited 0.095 gm. and 0.105 gm. of iodoform, or 0.14 and 0.16 moles, respectively, per mole of pyrogallol. The identification depended upon the characteristic odor of iodoform, and the proper melting point of 118° to 119°C. The only other precipitates observed were from oxidations carried out with 10-fold concentrations of iodine and pyrogallol at pH values drifting from 12 or 13 to 8 or less. These precipitates were jet black in color, did not melt below 300°C., and were not examined further.

"Oxidized Pyrogallol Solution"

Pyrogallol, 1.29 gm., or 0.01 mole, was added with stirring to 500 cc. of an aqueous solution containing 6.2 gm. of boric acid, 5.1 gm. of sodium hydroxide, and 2.59 gm. (0.01 mole) of iodine (added in potassium iodide solution). The mixture, whose pH was 12.0, immediately became red. This "oxidized pyrogallol solution" was kept at room temperature and under nitrogen for 30 min. to 2.5 hr. before use, and apparently did not change within the latter time.

Recovery of Pyrogallol Triacetate

An "oxidized solution" made 30 min. previously from 1.29 gm. of pyrogallol, was rapidly stirred with 5 cc. of acetic anhydride (3). A light cream-colored precipitate was obtained with a melting point of 163° to 164°C., undepressed by admixture with an authentic sample of pyrogallol triacetate, m.p. 164 to 165°C.; yield 2.29 gm. or 88.7%. A control experiment containing no iodine resulted in an 87% yield of the triacetate.

Aliquots, 10 cc., of a similar solution were removed before and after the addition of the acetic anhydride, and were discharged into 100 cc. of 1% sulphuric acid. The iodine in the mixtures was equivalent to 5.16 cc. and 11.6 cc., respectively, of 0.0324 *N* sodium thiosulphate. Since the blank containing neither acetic anhydride nor pyrogallol required 12.3 cc. of the thiosulphate, the recovery of iodine was 42% and 94%, respectively.

Recovery of Purpurogallin and Derivatives

(*a*) Pyrogallol, 1.89 gm. (0.015 mole) was dissolved in 400 cc. of water containing 1 gm. of sodium hydroxide, at room temperature and under nitrogen, and 150 cc. of 0.2 *N* iodine (0.015 mole) was added with stirring. The solution, pH 12.0, immediately became red-black in color, and after 10 min. gave a negative test for free iodine. Upon acidification with 10% sulphuric acid the color of the solution decreased considerably in intensity, and an orange, flocculent precipitate separated. After being washed and then dried *in vacuo*, the substance melted with decomposition at 264° to 268°C. Yield, 0.41 gm. or 25%. Recrystallization from toluene gave orange needles melting at 269° to 271°C., the value recorded for purpurogallin being 272° to 274°C. with decomposition (33).

A portion, 0.15 gm., was dissolved in 25 cc. of ethanol, and ether containing the diazomethane from 4 gm. of nitrosomethylurea was added. Next day the light yellow solution when evaporated to 50 cc. deposited 0.13 gm. (72%) of fine yellow needles, which when recrystallized from ether melted at 179° to 180°C. This melting point was 3°C. higher than the latest recorded value (18) and was not depressed by admixture with an authentic sample of 2′,3′,4-trimethyl purpurogallin.

(*b*) An "oxidized solution", made 2.5 hr. previously from 1.3 gm. of pyrogallol, was acidified with acetic acid, and extracted continuously with ether for about five hours. After being concentrated, the dark-red extract was evaporated to dryness at room temperature and *in vacuo* over sodium hydroxide. Acetic anhydride, 15 ml., and five drops of concentrated sulphuric acid were added to the red-black mass. After 30 min. without external heating, the mixture was poured into 300 cc. of ice and water, and 0.3 to 0.8 gm. of a yellow precipitate formed. Repeated crystallization from ether yielded orange prisms with the composition of a purpurogallin triacetate and melting at 162° to 163°C. This melting point agreed with that of the isomer considered by Thorn and Barclay (28) to be the 4,2′,3′-triacetate, although Haworth, Moore, and Pauson (19) recorded a melting point of 138° to 140°C. for this compound.

(*c*) An "oxidized solution", made 30 min. previously from 1.3 gm. of pyrogallol, was continuously stirred under nitrogen while 5 cc. of dimethyl sulphate was slowly added during a 30 min. period. This addition caused the color of the solution to increase and after four hours the pH had decreased from 12 to about 10. After acidification with acetic acid, the mixture was extracted continuously with ethyl acetate and the extract was distilled in steam. The hot aqueous residue in the still was filtered to remove a small amount of dark amorphous material, and the filtrate on cooling deposited 0.3 to 0.4 gm. of an orange-red substance. About one-fifth of this substance was high-melting, red in color, and insoluble in ether. The remaining four-fifths when recrystallized from ether gave shining, dark-red rosettes of monoclinic needles in a yield of 25 to 32% based on the pyrogallol, and melting at 194.5° to 195°C. Their composition was that of a monomethyl ether of purpurogallin, and their melting point was close to the value of 193°C. reported by Critchlow, Haworth, and Pauson for the 2′ isomer (7).

On one occasion orange yellow crystals of m.p. 194° to 195°C. were obtained in place of the dark red needles, but there was no depression of melting point when the two forms were mixed.

Oxidations of Vanillin with Hypoiodite (Table II, Fig. 2)

Solutions of 3.09 gm. of boric acid in 75 cc. volumes of water were mixed with the proper volume of *N* sodium hydroxide (10 cc. to 80 cc.) to obtain the desired pH. After dilution to about 150 cc. with distilled water, 50 cc. of 0.2 *N* iodine in potassium iodide (0.005 mole) was added. Vanillin, 0.127 gm. or 0.00083 mole, was introduced at zero time as an aqueous suspension; the total volume was diluted to 250 cc. and the vanillin dissolved almost immediately. Solutions between pH 10 and 11 (runs 6 to 9) were orange to light yellow in color and remained clear, while those between pH 12 and 13.5 (runs 10 and 11) were both clear and colorless. The consumption of iodine at various times was followed as in the oxidations of pyrogallol, but the end point was definite and easy to observe. Iodoform was isolated after 24 hr. by making the solutions strongly alkaline and extracting with two 50 cc. volumes of ether. After being dried and evaporated, the extracts from runs 1, 2, 3, and 4 yielded 0.05, 0.052, 0.041, and 0.019 gm., respectively, of iodoform, which was identified by its melting point and odor.

5-Iodovanillin

The borate buffer – iodine solution was made up exactly as described, 10 cc. of the sodium hydroxide solution being included to give pH 8.2, and the amount of vanillin was increased to 0.76 gm. or 0.005 mole. Titration of an aliquot acidified after 15 min. indicated 2.9% of unused hypoiodite, and the equivalent amount of sodium thiosulphate was added to the remainder. The solution was then acidified with 10% sulphuric acid; the resulting cream colored precipitate was washed well with water and dried. Yield, 1.25 gm. (90%), and melting point 177° to 179°C. Two recrystallizations from glacial acetic acid yielded pale yellow needles with the analytical composition of an iodovanillin, and with a melting point, 181° to 182°C., in agreement with the recorded value of 180°C. (9) for 5-iodovanillin.

The above experiment, when repeated with a borate buffer including 50 cc. of *N* sodium hydroxide to keep the pH at 10, yielded a solution with the deep red color of iodine. This color required 15 min. to fade to a pale orange. An aliquot, when acidified at this time and titrated, contained 31% of "free" iodine, which presumably originated from by-product iodate. The remainder of the solution yielded 0.87 gm. (62.7%) of 5-iodovanillin, melting at 171° to 175°C., raised to the correct value of 181°C. by recrystallization.

Rate of Oxidation of Pyrogallol with Hypochlorite (Table III, Fig. 3)

The chlorine obtained from the action of excess hydrochloric acid on 4 gm. of potassium permanganate was swept with nitrogen into 250 cc. of *N* sodium hydroxide to yield a stock solution approximately 0.2 *M* in chlorine. Some of this stock solution, 25 cc. (0.005 mole) was transferred to a dark brown, glass bottle containing 75 cc. of 0.67 *M* boric acid and the amount of *N* sodium

hydroxide to give the desired alkalinity. After the mixture had been diluted with distilled water to 225 cc. and had been brought to 25° ± 0.05°C., 0.11 gm. (0.00083 mole) of pyrogallol dissolved in 25 cc. of water at 25°C. was added.

The consumption of hypochlorite was followed by transferring 10 cc. aliquots into 100 cc. of water containing 0.1 to 0.2 gm. of potassium iodide; 10 cc. of 10% sulphuric acid and the starch indicator were added, and the liberated iodine was rapidly titrated with 0.025 *N* sodium thiosulphate solution. The end point was transitory.

Recovery of Trichloropyrogallol

A solution consisting of 200 cc. of 10% sodium carbonate and 25 cc. of 0.227 *M* chlorine (0.0058 mole) in *N* sodium hydroxide was added to 0.24 gm. (0.0019 mole) of pyrogallol dissolved in 25 cc. of water. Ten minutes later, when the hypochlorite was completely reduced, 1 gm. of zinc dust was added, the mixture (pH about 12) was acidified with 10% sulphuric acid, and was continuously extracted for 12 hr. with ether. Evaporation of the dried extract to 10 cc., followed by dilution with petroleum ether, caused the separation of 0.34 gm., (73%) of a white crystalline substance. When dried *in vacuo* over phosphorus pentoxide, this substance sintered markedly at 110°C. and melted at 179° to 180°C. with decomposition, as described for trichloropyrogallol monohydrate (1, 30). A sample was therefore dehydrated at 110°C. for 30 min. for analyses. Found: C, 30.9, 31.1; H, 1.51, 1.55; Cl, 45.7, 45.9%. Calc. for $C_6H_3O_3Cl_3$: C, 31.4; H, 1.3; Cl, 46.4%.

Recovery of 5-Chlorovanillin

(*a*) A suspension of 0.88 gm. of vanillin (0.0058 mole) in 100 cc. of water was mixed at room temperature with a solution composed of 75 cc. of 0.67 *M* boric acid, 25 cc. of *N* sodium hydroxide made 0.23 *M* (0.0058 mole) in chlorine, and 50 cc. of water. This mixture, pH 8.8, after 10 min. gave a negative test for hypochlorite. Acidification with 10% sulphuric acid then caused the deposition of 0.71 gm. of slightly yellow crystals, which sintered and darkened near 150°C. before melting to a red-black liquid at 158° to 162°C; yield, 65%. Solution in hot ethanol removed 70 mgm. of insoluble material, and the filtrate on cooling deposited pale yellow plates with the methoxyl and chlorine content of a chlorovanillin. The melting point of 163° to 164°C. was correct for the 5-chloro isomer (20), and admixture with an authentic sample of 5-chlorovanillin did not depress this value.

(*b*) The preparation in (*a*) was repeated with the exception that 45 cc. of *N* sodium hydroxide was substituted for the 50 cc. of water included in the mixture. This change altered the pH to 12.0, and one hour elapsed before the solution gave a negative test for hypochlorite. Acidification caused the precipitation of 0.46 gm. (41%) of 5-chlorovanillin melting at 158° to 162°C., undepressed by admixture with an authentic sample.

A red, flocculant precipitate immediately formed when the acidified mother liquor was mixed with 100 cc. of a saturated solution of 2,4-dinitrophenylhydrazine. After recovery, this precipitate weighed 0.92 gm. (39%), melted at 256° to 258°C., and contained no chlorine. Recrystallization from ethanol gave

dark red crystals of vanillin 2,4-dinitrophenylhydrazone with the correct methoxyl content and the correct melting point of 264° to 265°C., not depressed by admixture with an authentic sample.

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THE SILVER CATALYZED OXIDATION OF ETHYLENE[1]

I. SLOW PROCESSES ON THE CATALYST SURFACE

By A. Orzechowski[2] and K. E. MacCormack

ABSTRACT

In the silver catalyzed oxidation of ethylene or ethylene oxide (EtO), the silver catalyst activity measured under constant standard conditions in a flow system was found to be dependent on the conditions of previous catalyst treatment such as reaction temperature and reactant composition. The results are explained on the basis of slow establishment of equilibrium respecting fixation of stably sorbed oxygen atoms and surface products of oxidation. It is emphasized that in view of the slow processes observed, the kinetic measurements must be punctuated by frequent stabilizing check runs in order to maintain the catalyst in the same reference state.

INTRODUCTION

This publication is the first of a series concerning the oxidation of ethylene on a silver catalyst. Part I presents the observations on slow processes which occur after changes of operating conditions during catalysis. Part II will deal with the kinetics of C_2H_4 oxidation and Part III with the kinetics of ethylene oxide (EtO), oxidation, and its isomerization to acetaldehyde. Part IV will be concerned with reaction mechanism.

A separate presentation of the slow processes which have been observed during the catalytic oxidation of C_2H_4 and which appear to be dependent on the conditions of pretreatment of the silver catalyst by the reacting gas mixture is considered useful from two main points of view. Kinetic measurements carried out under circumstances which fail to recognize the existence of slow processes cannot be deemed reliable for purposes of mechanism interpretation.

With the exception of the initial conditioning period, studied by Murray (5), very little has been reported in the literature concerning these effects. It is intended to emphasize the influence of catalyst "history" on its subsequent activity and the fact that true kinetics can only be observed on a silver surface soon after a standardized pretreatment which maintains the catalyst in the same reference state. This is opposed to observations made when true equilibrium is attained after very prolonged reaction with attendant changes in the nature of the catalyst.

EXPERIMENTAL

The flow apparatus and the single sample of catalyst, used throughout, will be described in Part II. Few experimental details will be mentioned here.

Having mounted the silver catalyst in the reactor, it was maintained in a N_2 atmosphere, when not in service. In beginning operations, it was heated in a N_2 stream to the desired temperature, then O_2, followed by C_2H_4 or EtO,

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[2] *National Research Council Postdoctorate Fellow, 1951–1953.*

was admitted at the desired flow rates. For close-down operations the reverse order was observed. When the flow rate or partial pressure was changed, it was always done quickly and in such a way as to keep the C_2H_4 concentration to a minimum during the change.

Except for the first conditioning period (Fig. 1), the catalyst remained in continuous operation over periods of weeks, with temperature control better than $\pm 0.5°$ C., and flow rates constant to 1%.

The composition of the off-gas with respect to EtO and CO_2 was measured with an accuracy of $\pm 2\%$ of the absolute value. In the absence of catalyst, no products could be detected at 234° C.

The working pressure was atmospheric. Unit feed flow rate was arbitrarily set at 41.8 liters (N.T.P.)/hour of gas mixture. The following feed compositions were used, expressed by symbols which are described here and maintained throughout the forthcoming publications. The symbol pE_nO_m indicates a mixture flow rate of 41.8 p liters/hr., with C_2H_4 and O_2 contents, $2.35n\%$ and $9.90m\%$ respectively, the remainder being N_2. Thus, E_2O_2 corresponds approximately to a mixture of air–C_2H_4 of ratio 20: 1. X used instead of E refers to EtO.

A. Oxidation of C_2H_4

Feed $1E_2O_2$: 4.70% C_2H_4, 19.8% O_2, 75.5% N_2.

B. Oxidation of EtO

Feed $1X_2O_2$: 4.70% EtO, 19.8% O_2, 75.5% N_2.

C. Isomerization of EtO

Feed $1X_2O_0$: 4.70% EtO, 95.30% N_2.

The silver catalyst sample was estimated, on the basis of B.E.T. adsorption measurements using similar catalyst, to have a surface area of the order of 6 sq. meters and oxygen adsorption capacity in the order of 1 cc. (N.T.P.) at the working temperatures.

All the gases used were obtained from commercial cylinders. The EtO was manufactured by the Matheson Company with a specified purity of 99.5%. The authors are indebted to Dr. F. P. Lossing for mass spectrometric analysis of this gas which confirmed the absence of impurities other than possibly 3% of N_2. Ohio "Medical Grade" C_2H_4 with a specified purity of at least 99.5% and Dominion Oxygen Company nitrogen and oxygen, with a guaranteed purity of 99.7% in each case, were used.

RESULTS

A. Oxidation of Ethylene

1. The Conditioning Period

The conditioning period at reaction temperature 234° C., (feed $1E_2O_2$) is shown in Fig. 1. The conversion to EtO goes through a maximum; the conversion to CO_2 decreases, and the selectivity* increases. At least 150 hours are needed for approximate stabilization. The scattering of data is due to imperfections in the process control, which were eliminated at the end of this period.

* *Selectivity = % C_2H_4 converted to EtO/total % C_2H_4 reacted.*

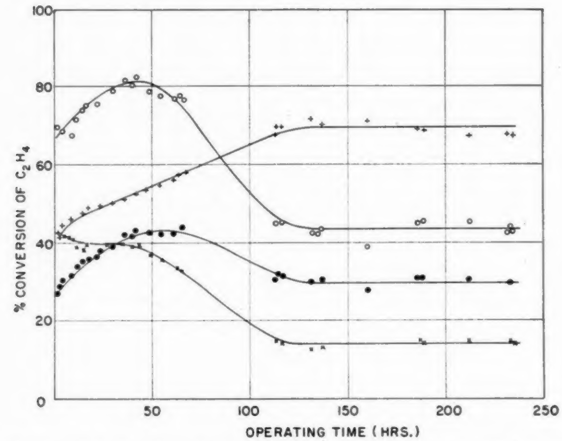

FIG. 1. Oxidation of C_2H_4. Conditioning period of new catalyst. 234° C. Feed $1E_2O_2$. ● Conversion to EtO; × conversion to CO_2 and H_2O; ○ total conversion; + selectivity.

2. *Slow Processes Due to Change of Temperature Level, (Feed $1E_2O_2$)*

If the operating temperature is changed upwards from 234 to 274° C. (see Fig. 2), the conversion slowly increases and selectivity decreases. The reverse occurs when the temperature level is reduced.

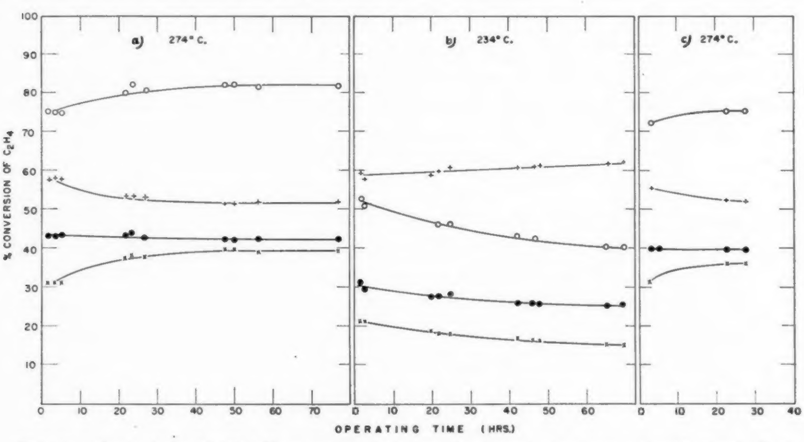

FIG. 2. Oxidation of C_2H_4. Slow processes due to changes of temperature level. Feed $1E_2O_2$. (*a*) After conditioning period at 234° C.; (*b*) after (*a*); (*c*) after (*b*). ● conversion to EtO; × conversion to CO_2 and H_2O; ○ total conversion; + selectivity.

3. *Slow Processes Due to Change of Flow Rate (at Constant Temperature 274° C.)*

Numerous observations were made after changes of flow rate extending between twofold and 16-fold. When the flow rate is increased, EtO and CO_2

formations decrease slowly, the latter decrease being of greater magnitude than the former with resulting increase in selectivity. The reverse is true when the change of flow rate is in the opposite direction. This drift in conversions becomes very slow after 24 hr. at the new flow value.

A typical case was as follows: after feeding $4E_4O_2$ the flow rate was decreased fourfold; three hours after the change the conversions were CO_2 23.5%; EtO 27%; selectivity 53.5%; 20 hr. later CO_2 26.5%; EtO 28.5%; selectivity 51.9%.

4. *Slow Processes Due to Change of Feed Composition (at Constant Temperature and Flow Rate)*

A striking change in catalyst behavior is caused by its pretreatment with an ethylene-rich feed (E_4O_1). The effect is the same at 234° C. and 274° C. and consists in substantially permanent lowering of EtO and increase of CO_2 production.

The conversions for the standard $1E_2O_2$ feed at 234° C. were: before runs E_4O_1: EtO 17.0%: CO_2, 10.5%: selectivity, 62%; after runs E_4O_1: EtO, 13.5%: CO_2, 12.0%: selectivity, 53%.

This effect lasted more than 200 hr. at 235° and is difficult to remove completely, although the passage of feeds enriched in O_2 is very helpful. It is easier to restore the surface activity when the same poisoning has occurred at 274° C.

With the knowledge of slow processes obtained at this stage, the kinetic runs for C_2H_4 oxidation were made at 274 and 234° C. Data will be presented in Part II.

5. *Slow Processes Due to Pretreatment of Catalyst by O_2 or by EtO and O_2*

Six runs with the standard $1E_2O_2$ feed at 274° C. are shown in Fig. 3. These data were obtained following a series of pretreatment variables listed in the table below. The numbers in brackets indicate the order in which they were

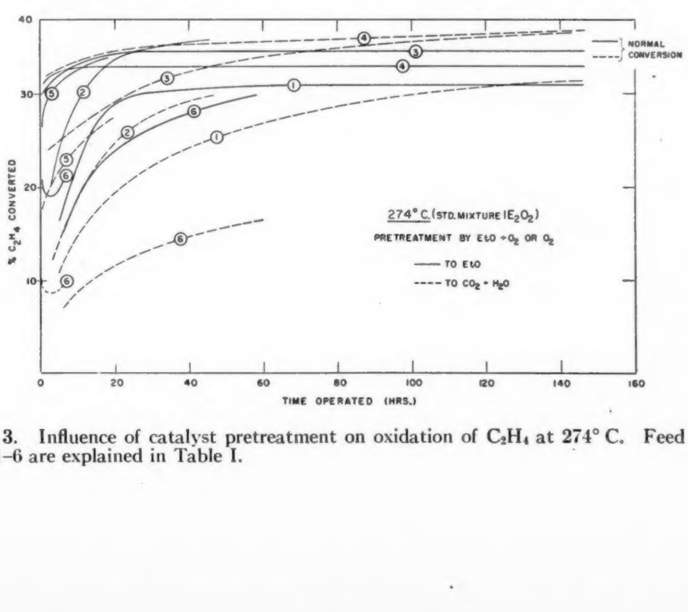

FIG. 3. Influence of catalyst pretreatment on oxidation of C_2H_4 at 274° C. Feed $1E_2O_2$. Runs 1–6 are explained in Table I.

performed for each experiment. The experiments numbered in column 1 are likewise in chronological order.

In each of the experiments 1–6 listed above involving final pretreatment by O_2 or by EtO + O_2, the standard ethylene oxidation runs resulted in abnormally low conversion and high selectivity. This effect diminished slowly during prolonged operation with the standard feed gas. The first experiment may include some influence of temperature change, but this was absent in the subsequent ones. It is noteworthy that pretreatment by oxygen alone (Curve 3) caused considerable poisoning, though this may be explained by the influence of EtO + O_2 employed in Experiment 2, which may not have been eliminated at that time. In support of this, further oxygen treatment in Experiment 4, where little influence could be attributed to previous treatment by EtO + O_2, produced a relatively minor effect on the standard ethylene oxidation. The break in continuity of Curve 6 was caused by cooling the reactor to room temperature in a stream of N_2 after five hours' operation.

6. *Slow Processes Due to Pretreatment of Catalyst by EtO + N_2 (X_2O_0)*

Fig. 4 shows the results of two experiments, 7 and 8, details for which are given in the table. The continuity of Curve 7 was interrupted at A by cooling to room temperature in a N_2 stream, and subsequently at B by accidental temperature drop to 250° C. for three hours.

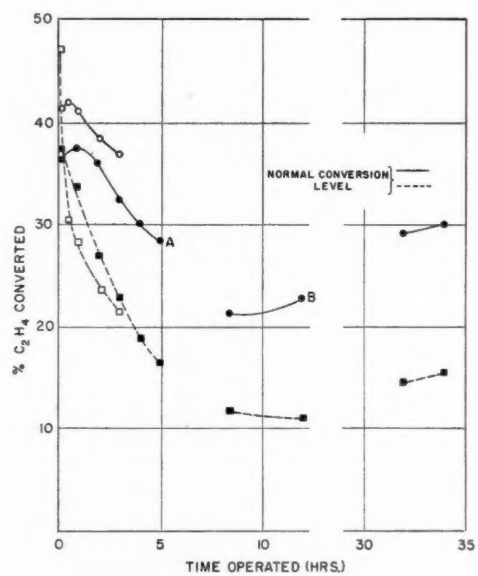

FIG. 4. Influence of catalyst pretreatment on oxidation of C_2H_4 at 274° C. Feed $1E_2O_2$, with pretreatment by EtO + N_2. ——— Conversion to EtO; - - - conversion to CO_2 and H_2O; ■ ● Expt. 7; □ ○ Expt. 8 (see Table I).

The feature of pretreatment by EtO + N_2 is an anomalous high level of conversion which decreases rapidly to the low poisoned level, followed by slow recovery.

B. Oxidation of Ethylene Oxide

1. Oxidation of EtO after pretreatment by C_2H_4 oxidation ($1E_2O_2$).

The results are shown in Fig. 5 for the feed, $1X_2O_2$, admitted after the following operations at 274° C.

Run I: pretreatment by Expt. 4 of Fig. 3
Run II: " " " 5 " Fig. 3
Run III: " " " 7 " Fig. 4

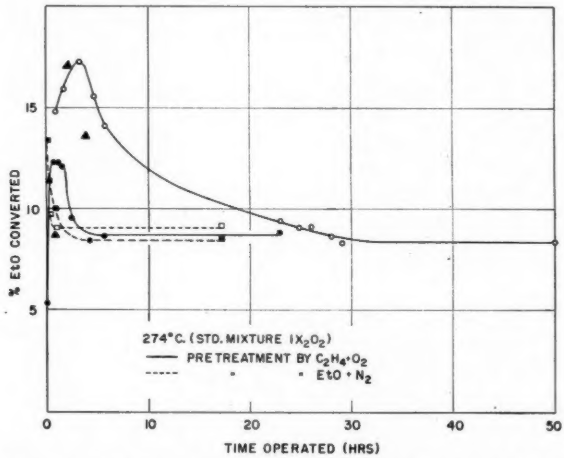

FIG. 5. Influence of catalyst pretreatment on oxidation of EtO at 274° C. Feed $1X_2O_2$. Pretreatment by C_2H_4 oxidation: runs I (▲), II (○), III (●). Pretreatment by EtO + N_2: runs A (□), B (■). (See Table I.)

The common feature of these results is that the conversion of EtO to CO_2 and H_2O goes through a maximum before a steady state is obtained.

2. Oxidation of EtO after pretreatment by EtO + N_2 (feed X_2O_0).

The results are shown in Fig. 5 for the feed $1X_2O_2$ admitted after the following operations at 274° C.

Run A: 1.5 hr. pretreatment by X_2O_0, which followed prolonged kinetic runs at EtO oxidation (see Table I, Expt. 6).

Run B: 28 hr. pretreatment by X_2O_0 which followed run A (see Table I, Expt. 6).

Characteristic of pretreatment by EtO + N_2 is the rapid decrease of the oxidation of EtO to a stable value.

DISCUSSION

The importance of these results lies in their influence on the correct establishment of the reaction kinetics. It became evident almost from the beginning

TABLE I

PRETREATMENT VARIABLES (ALL AT 274° C., EXCEPT WHERE OTHERWISE STATED)

Experiment No.	Pretreatment				Reference for standard $1E_2O_2$
	$C_2H_4 + O_2$	$EtO + O_2$	$EtO + N_2$	O_2	
1	(1) Kinetic series 234° C.	(2) 5 hr.		(4) 40% $O_2 + N_2$ 20 hr.	(3) 234°, poisoned (5) Curve 1, Fig. 3
2		(1) 1.5 hr.		(2) 18 hr.	(3) Curve 2, Fig. 3
3				(1) 67 hr.	(2) Curve 3, Fig. 3
4				(1) 35 hr.	(2) Curve 4, Fig. 3
5		(1) 5 hr. (Run I, Fig. 5)			(2) Curve 5, Fig. 3
6		(1) Run II, Fig. 5 and kinetic series	(2) 1.5 hr.		
		(3) 18 hr. (Run A, Fig. 5) (5) 46 hr. (Run B, Fig. 5)	(4) 28 hr.		(6) Curve 6, Fig. 3
7			(1) 18 hr.		(2) Curve 7, Fig. 4
8		(1) 23 hr. (Run III, Fig. 5)	(2) 3 hr.		(3) Curve 8, Fig. 4

of this work that reliable data could not be obtained unless care were taken to maintain a standard state for the catalyst. Also, if the kinetics for EtO oxidation are to be correlated with those of the C_2H_4 oxidation, account must be taken of the fact that the catalyst conditioned for one reaction is certainly in an unsteady state with respect to the other.

It is suggested that the concept be introduced of separate rates of attainment of surface equilibrium to account for coverage (*a*) by reacting substances and (*b*) by substances which are nonreactive.

Nonreactive species behaving as poisons or moderators may be more stably sorbed either on the surface or within the silver lattice than reacting species. Oxygen atoms are known to diffuse and dissolve in silver (6). Surface substances could act as poisons simply by virtue of the space occupied whereas both lattice and surface substances may act as impurity centers with energetic effects which virtually alter the extent of the catalyst surface. Extremely small traces of bulk impurities are known to modify the electronic and catalytic properties of metals (3, 4).

On this basis the relations for the rate of establishment of equilibrium for reacting species on the free Ag surface may now be developed. The stoichiometry of the reactions is neglected for simplicity.

Let R = reaction rate

V = net adsorption rate for reactants (adsorption minus desorption rate)

Δq = change in quantity of reactants accumulated on surface which contribute to coverage during time, t.

q_0 = maximum possible amount of adsorbed reactants in the absence of poisoning effects.

Subscripts are used as follows:

e refers to reactant equilibrium coverage for a given poisoning level;

t refers to conditions at time, t;

av refers to average values over the time, t.

At equilibrium $V_e = R_e$.

Since $V_{av} > V_e$,

then

[1] $$V_{av} > R_e.$$

[2] $$\Delta q = (V_{av} - R_{av})t\,.$$

From [1] and [2] it follows

[3] $$\Delta q > (R_e - R_{av})t\,.$$

[4] Since $$R_{av} < R_t < R_e$$

[5] and $$\Delta q < q_0\,,$$

from [3], [4], and [5] we have

[6] $$R_t < R_e < R_t + q_0/t\,.$$

In the present case q_0 is in the order of 1 cc. (N.T.P.). At time t = 0.1 hr., R_t is already found to be in the order of 400 cc. (N.T.P.)/hr. and equation [6] may therefore be written,

$$R_t = 400 < R_e < 410 \text{ cc./hr.}$$

Hence the equilibrium coverage in question is certainly very closely approached within the first 0.1 hr.

Slow processes which continue for times in the order of 100 hr. or more cannot be identified with the establishment of equilibrium surface coverage by reacting species and must be attributed to establishment of equilibrium respecting poisons. In view of the large difference in the magnitude of these two rates, reaction kinetics may be studied on a poisoned catalyst surface, provided the same degree of poisoning is maintained throughout. This requirement was observed during all the measurements reported in Parts II and III, by preconditioning the catalyst at a given temperature with a gas mixture of average composition respecting the range employed. Frequent checks were made to verify the maintenance of the same reference state.

It is believed that stable poisons accumulate slowly during reaction and that for any given level of poisoning the remainder of the surface is available for rapid establishment of equilibrium respecting reacting species. A change in temperature or composition of the reactants will tend to affect the extent of poisoning in a direction dependent on the equilibrium position for the new system respecting poisons.

At first sight it may appear that where conversion of reactants exceeds the normal level, as for example, the case of C_2H_4 oxidation during the first few

hours following treatment by EtO and N_2 (Fig. 4), it could be attributed to slow burning of carbonaceous deposit on the surface. However, calculation based on the estimated adsorption capacity of the catalyst sample shows that to account for the excessive CO_2 formation the carbon deposit would have to be several hundred atoms thick. Run 8, Fig. 4, shows during the first three hours an average conversion to EtO of 39% instead of the maximum of about 33% expected on the basis of curves for the preceding group of runs shown in Fig. 3. With feed flow equal to 41.8 liters (N.T.P.)/hr. containing 4.7% C_2H_4, at least 350 cc. of excess EtO are formed whereas the surface adsorption capacity is of the order of 1 cc. Hence the changes in conversion cannot be explained on the basis of massive desorption only.

It remains to deduce the nature of the inhibiting species which are responsible for observed slow processes.

(1) *Inhibition of Ethylene Oxidation by O_2 and by Residues Formed During Oxidation of EtO*

Pretreatment by O_2 or by EtO + O_2 (see Table I, Expts. 1–6 inclusive) results in the qualitatively similar observation that conversion both to CO_2 and EtO is abnormally low and selectivity high for standard conditions with a tendency to approach normal values with time. In addition to these, similar effects on the C_2H_4 oxidation are produced by pretreatment (*a*) at a higher flow rate and (*b*) at lower temperature with the same flow rate and composition of feed composed of C_2H_4 and O_2. The converse is also true.

The only common feature of all these pretreatments is that O_2 concentration in the off-gas is higher than in the case of standard run $1E_2O_2$, whose behavior they affect. However, according to Fig. 3, oxygen alone is a less active inhibitor than EtO + O_2 and the influence of O_2 decreases when the inhibition by EtO and O_2 is removed; on the other hand, EtO alone (with N_2) not only fails to poison, but enhances activity (Fig. 4). Hence it must be concluded that there are two inhibiting species:

(1) Oxygen atoms, slowly attaining stable positions.

(2) Slowly formed surface products of EtO oxidation.

Explanation (1) respecting oxygen action may be applicable to the observation of Benton and Elgin (1) that pretreatment of silver by O_2 always gave lower activity for H_2 oxidation than pretreatment by H_2.

Fig. 4 may now be explained. After the initial high conversion, which results from the removal of inhibiting oxygen by EtO + N_2 pretreatment, oxygen is slowly sorbed again with a drop in conversion to the former level probably determined by unremoved products of former EtO oxidation. The latter were not removed by runs prior to EtO + N_2. Then these also are slowly eliminated.

(2) *Influence of Pretreatment on EtO Oxidation*

In the case of pretreatment by EtO + N_2 the conversion of EtO to CO_2 is initially high and then decreases (Fig. 5, A, B). This conforms to the hypothesis that inhibiting particles are O atoms and EtO surface oxidation products.

If the pretreatment is C_2H_4 oxidation, the conversion of ethylene oxide to CO_2 goes through maximum (Fig. 5: I, II, III). Runs for C_2H_4 and for EtO

oxidation differ largely in the absence of C_2H_4 and in higher concentration of EtO and O_2 in the latter runs. To explain the ascending portion before the maximum, it is therefore necessary to conclude that there is a third sort of stably sorbed particle formed during C_2H_4 oxidation. When EtO oxidation is started, these are at first removed, followed by the onset of oxygen inhibition and formation of EtO oxidation residues.

It may be noted here that Twigg (7) found the formation of residues on contact with oxygenated catalyst much greater in the case of EtO than in the case of C_2H_4.

(3) *Inhibiting Effect of Pretreatment by Feed Rich in C_2H_4 and Poor in O_2 Standard C_2H_4 Oxidation*

When the standard feed $1E_2O_2$ is passed after pretreatment by E_4O_1, initial measurement shows higher CO_2 and lower EtO conversions with lower selectivity than for normal conversion values. All these values tend to approach the normal level slowly with time.

The essential difference between E_4O_1 and $1E_2O_2$ is that the former has much lower O_2 and much higher C_2H_4 concentration in the outgas. The effect with respect to CO_2 conversion and to selectivity conforms well to the picture of inhibiting oxygen having been removed by an oxygen-deficient run. However, the decrease in conversion to EtO can only be understood if the formation of stable residues during C_2H_4 oxidation is assumed, as discussed in the previous section. The latter effect may be considered similar to that observed by Benton and Elgin (2); in the oxidation of H_2 the use of mixtures with large H_2 excess resulted in subsequent permanent decrease of catalytic activity. This could be due to fixation of H_2O or OH' in stable positions.

The slow processes which were found must therefore be attributed to the slow fixation and removal of three kinds of particles: oxygen atoms, surface products of C_2H_4 oxidation, and surface products of EtO oxidation.

These effects may be compared with known poisoning effects due to Cl_2 or SO_2. Both decrease the conversion*, the selectivity being higher than the normal selectivity extrapolated to zero contact time in the case of Cl_2, lower than normal in the case of SO_2. Obviously, this behavior cannot be due to the reduction of effective contact time by poisoning, as was suggested during discussion of Twigg's work (7). Rather, the conversion and selectivity changes are due to the formation of stably sorbed Cl_2 and SO_2 particles—impurity centers—which change the coverage and possibly the energetics of the catalyst system.

The investigation was not carried beyond this stage by virtue of large time consumption and the fact that a sound basis for kinetic measurements had been achieved.

SUMMARY

In the silver catalyzed oxidation of ethylene or ethylene oxide (EtO), the silver catalyst activity measured under constant standard conditions in a

* *According to some preliminary work in this laboratory, this effect is reversible, the time needed for recovery being of the same order as in the case of slow processes discussed in this paper.*

flow system was found to be dependent on the conditions of previous catalyst treatment such as reaction temperature and reactant composition.

Oxidation of C_2H_4

Stabilization of new catalyst by an C_2H_4–O_2 mixture under standard conditions, referred to as (I) was found to occupy a period of about 150 hr. If this is followed by some other nonstandard conditions (II) a subsequent return to (I) will produce an abnormal activity (A), the effect being removed within a period of 50–200 hr., depending on II.

The following correlations were established between (II) and (A):

(*a*) (II) is the standard C_2H_4–O_2 mixture at lower (or higher) temperature than that used in (I).

(A) shows lower (or higher) conversions and higher (or lower) selectivity respecting EtO formation.

(*b*) (II) is an C_2H_4–O_2 mixture of high C_2H_4 and low O_2 concentration.

(A) shows increased CO_2 and decreased EtO formation; difficult to eliminate completely.

(*c*) (II) is O_2 or a mixture of O_2 and EtO.

(A) shows pronounced activity decrease with increased selectivity.

(*d*) (II) is EtO.

(A) shows high conversions rapidly declining.

Oxidation of EtO

The catalyst has to be stabilized under standard conditions by a mixture of EtO–O_2. Slow processes occur similar to those observed during C_2H_4 oxidation:

(*a*) (II) is EtO.

(A) shows abnormally high conversion to CO_2, rapidly decreasing.

(*b*) (II) is an C_2H_4–O_2 mixture.

(A) indicates that conversion to CO_2 passes through a maximum with time.

The results are explained on the basis of slow establishment of equilibrium respecting fixation of stably sorbed oxygen atoms and surface products of oxidation. It is emphasized that in view of the slow processes observed, the kinetic measurements must be punctuated by frequent stabilizing check runs in order to maintain the catalyst in the same reference state.

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EXCITED MOLECULES AS THE REACTIVE SPECIES IN ACTIVE NITROGEN[1]

By R. A. Back, Margaret Menzies, and C. A. Winkler

ABSTRACT

No reaction has been detected between ethylene and nitrogen molecules obtained in the thermal decomposition of metallic azides. Since such decomposition reactions apparently produce nitrogen molecules excited to the same electronic level as those present in active nitrogen formed by a condensed discharge, it might be inferred that excited molecules are not the reactive species in active nitrogen.

INTRODUCTION

When nitrogen is passed through a condensed discharge under suitable conditions, its chemical reactivity is greatly enhanced. Strutt (7) attributed the reactivity to nitrogen atoms, but it has also been ascribed to N_2^* excited molecules, N_3 radicals, N_2^+ ions, and other species. Mitra has reviewed the various arguments and evidence (5); in a recent paper (6) he concludes that nitrogen atoms are probably the active species.

It is generally agreed that nitrogen atoms are formed in the discharge and recombine to form nitrogen molecules in the metastable $B^3\Pi_g$ state, mostly excited to the 11th or 12th vibrational level. These may redissociate, or may undergo transition to an $A^3\Sigma_u^+$ state with emission of the first positive band, corresponding to the persistent yellow afterglow associated with active nitrogen. Transition from the $A^3\Sigma_u^+$ state to the ground state results in emission of Vegard-Kaplan bands in the far ultraviolet. Both excited species are probably subject to radiationless transition to the ground state through a suitable third body collision.

A source of excited nitrogen molecules other than the electrical discharge would obviously be of assistance in identifying the reactive species in active nitrogen. The thermal decomposition of certain metallic azides seems to offer such a source. The results of kinetic studies by Thomas and Tompkins (8, 9) on the thermal decomposition of barium azide appear to be satisfactorily explained on the basis of recombination of N_3 excitons to form N_2 molecules, while the formation of atomic nitrogen appears to be excluded. Other studies by Audubert (1) and by Finkelstein (3) indicate that at least part of the nitrogen formed during decomposition of various metal azides is in an excited state. Strong excitation of the mercury resonance line in the presence of decomposing azides was observed, and interpreted in terms of a resonance transfer between nitrogen and mercury in the 1650 Å region, corresponding approximately to 173 kcal. per mole, and roughly to the $B^3\Pi_g$ state of the nitrogen molecule without vibrational excitation (4). It may be inferred, therefore, that the

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thermal decomposition of azides should provide a source of excited nitrogen molecules, unaccompanied by nitrogen atoms.

Since the reaction of ethylene with active nitrogen from a discharge tube has been found to occur rapidly, with production of hydrogen cyanide (10), it seemed of interest to decompose metallic azides in the presence of ethylene and examine the reaction products for hydrogen cyanide and other possible evidence for reaction between excited molecules of nitrogen and ethylene.

EXPERIMENTAL

Barium azide was prepared by distilling hydrazoic acid from a 3% solution into a suspension of barium hydroxide. The azide was precipitated with alcohol, filtered, and dried over concentrated sulphuric acid. Silver azide was precipitated by the addition of silver nitrate to sodium azide in aqueous solution, filtered, and dried in the same way. Both azides were used without further purification.

The azides were decomposed in a horizontal furnace made of 18 mm. Pyrex tubing. The azide was introduced in a boat, 12 cm. long, made of 14 mm. Pyrex tubing, open at both ends, and with a hole in the middle through which the azide was added.

Reaction rates were measured by rate of pressure increase, assumed to be due entirely to nitrogen evolved. Condensable products were analyzed for hydrogen cyanide by absorption in 1 N potassium hydroxide solution and titration with 0.01 M silver nitrate. A cupric acetate – benzidine acetate spot test was also used (2).

The decomposition of barium azide (50 to 175 mgm.) was studied in 17 experiments at 158° C. In 10 of these, ethylene was present at pressures ranging from 3 to 29 cm. The solid residue in the boat was dissolved in standard acid and spot tests were made for cyanide and ammonia, which would be formed if nitride were present in the residue. One aliquot portion of the solution was titrated with standard alkali to determine the amount of barium and ammonia present; a second aliquot was made alkaline, the ammonia boiled off, and the solution back titrated. The difference in titer value for the two aliquots allowed the amount of barium nitride formed during decomposition to be estimated.

Three experiments were made in which barium azide was dropped through a vertical furnace at 450° C. containing ethylene at a pressure of about 30 cm. Both gaseous products and solid residue were examined for the presence of hydrogen cyanide.

Three experiments were made with sodium azide and three experiments with silver azide in the presence of ethylene at temperatures of 360° C. and 300° C. with pressures ranging from 2 to 10 cm. and 8 to 20 cm. respectively. Analysis was made only for hydrogen cyanide in the condensable gaseous products and solid residue.

One experiment was made with each of ethylene, hydrogen, nitrogen, and helium to determine the effect on the rate of production and yield of nitrogen from barium azide at 158° C., with 13 cm. pressure of gas present.

RESULTS AND DISCUSSION

Hydrogen cyanide was not detected in either the condensable gaseous products or the solid residue from any of the experiments. For a 100 mgm. sample of azide, it should have been possible to detect conversion into cyanide of 0.1% of the nitrogen evolved.

The presence of ethylene during the decomposition of barium azide caused a decrease in both the rate of production and the yield of nitrogen, directly proportional to the pressure of ethylene. However, the recovery of ethylene and barium (2 to 4% as nitride) was complete. With hydrogen present, the decrease in rate of production and yield of nitrogen was much greater than with ethylene present, while nitrogen and helium had very little effect. The observed decrease in yield of nitrogen was much more than would correspond to complete conversion of the azide to nitride. A quantitative study of the behavior was not attempted but the results indicate that further studies of similar type might be interesting.

For a given preparation of azide the induction period was increased with increased ethylene pressure. Crystal size varied with each batch of azide prepared and the largest crystals had the shortest induction period. No measurable amounts of water were obtained following decomposition of the barium azide and the samples were assumed to be anhydrous. This was verified when the crystals were examined under a microscope and found to be monoclinic rather than triclinic.

With sodium and silver azides the yields of nitrogen corresponded to their complete decomposition and ethylene was totally recovered, although the rate of decomposition decreased with increased ethylene pressure. With none of the azides did an increase of temperature, after the reaction had stopped, cause further production of nitrogen.

The absence of hydrogen cyanide and other possible products of a reaction between active nitrogen and ethylene might be interpreted in several ways. It might, for example, be questioned that excited nitrogen molecules were produced in concentrations sufficient for chemical detection. While Finkelstein (3) has demonstrated the presence of excited nitrogen molecules in azide decompositions, through a study of energy transfers with mercury and other metallic vapors, a quantitative estimate of their concentration is rather difficult. However, for the consecutive processes of transfer and fluorescence,

$$N_2^{**} + Hg \longrightarrow Hg^{**} + N_2$$
$$Hg^{**} \longrightarrow Hg^{*} + h\nu_1$$
$$Hg^{*} \longrightarrow Hg + h\nu_2\ (2537\ \text{Å})\ .$$

Finkelstein calculated a lower limit of 3.5×10^{-8} for the over-all efficiency of conversion to 2537 Å radiation on the assumption that every molecule of nitrogen was excited. These calculations are rather crude, but they do suggest that an appreciable fraction of the nitrogen evolved must be in an excited state, probably sufficient for detection by the methods used if reaction between the excited nitrogen molecules and ethylene were possible.

It might also be suggested that, if the nitrogen is released mostly at the azide–metal interface (8, 9), it would have to diffuse through the lattice to

reach the ethylene in the gas phase, and might suffer de-excitation in the process. However, the efficiency of transfer and fluorescence found by Finkelstein would seem to indicate that an appreciable quantity of excited nitrogen does reach the gas phase to effect energy transfer with mercury. Furthermore, in the present experiments in which barium azide was dropped through ethylene at 450° C., well above its detonation temperature, de-excitation of the nitrogen before contact with ethylene seems unlikely.

Interpretation of the present experiments must also recognize that excited molecules derived from recombination of atoms formed in a condensed discharge through nitrogen are generally believed to be in the 11th or 12th vibrational level of the $B^3\Pi_g$ state, while those obtained by thermal decomposition of azides are possibly in the same electronic state but vibrationally unexcited. The difference in energy would amount to about 52 kcal. per mole (4). Hence, the reactions of ethylene with excited molecules from the two sources could differ energetically to this extent.

It would seem, however, that reaction of excited molecules from azide need not be energetically improbable because of this difference. This may be illustrated by considering a reaction of the type that appears to be encountered in the reaction of ethylene with active nitrogen from a discharge tube (10),

$$C_2H_4 + N_2^* \longrightarrow HCN + CH_3 + N.$$

If the excited molecule involved in the reaction is one formed by recombination of atoms from a discharge through nitrogen, the energy required to break the $N\equiv N$ bond involved may be taken as zero. If the $C=C$ bond dissociation energy is taken as 120 kcal. per mole and that of the $C\equiv N$ bond as 175 kcal. per mole, the reaction indicated would be some 55 kcal. per mole exothermic. If, on the other hand, the excited nitrogen molecule involved were derived from azide the reaction would be about 52 kcal. per mole more endothermic, i.e., approximately thermoneutral. Hence, although a difference in rate of reaction of active nitrogen derived from the two sources might be expected, energetic considerations alone do not appear to rule out the possibility of reaction between ethylene and active nitrogen obtained from azides, particularly in the experiments at higher temperatures.

Possible reactions other than that suggested above might well be more favorable energetically, as for example,

$$C_2H_4 + N_2^* \longrightarrow 2HCN + H_2$$

or

$$C_2H_4 + N_2^* \longrightarrow (CN)_2 + 2H_2 .$$

The various observations and arguments outlined above indicate, although they do not prove, that excited molecules of nitrogen are incapable of reactions of the type observed with active nitrogen from a discharge tube, and that the chemically reactive species in active nitrogen is not the excited nitrogen molecule.

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PREPARATION OF SOME NEW BRANCHED-CHAIN CARBOHYDRATES FROM D-α-FRUCTOHEPTONIC LACTONE[1]

BY R. J. WOODS[2] AND A. C. NEISH

ABSTRACT

D-α-Fructoheptonic lactone (I) was oxidized with an equimolar amount of periodic acid to give formaldehyde and a hexuronic lactone (II) which was hydrolyzed to crystalline 4-*C*-hydroxymethyl-L-xyluronic acid (III), (68% yield). Hydrogenation of III gave an aldonic acid which was isolated as crystalline 2-*C*-hydroxymethyl-L-xylonic lactone (V). Reduction of V by sodium amalgam gave 2-*C*-hydroxymethyl-D-xylose (VI), which crystallized after purification as the 2,5-dichlorophenylhydrazone. Hydrogenation of VI gave 1,1-di(*C*-hydroxymethyl)-D-threitol (VII) which was purified as the crystalline hexaacetate. Treatment of III with methanolic hydrogen chloride gave a glassy material which was reduced by sodium borohydride and hydrolyzed by hydrochloric acid to give 4,4-di(*C*-hydroxymethyl)-D-threose (IX), which was isolated and characterized as the crystalline 2,5-dichlorophenylhydrazone. Oxidation of III by either bromine or nitric acid gave 2-*C*-hydroxymethyl-D-xylaric acid (IV), which was characterized as the crystalline ammonium salt.

INTRODUCTION

The structure of D-α-fructoheptonic lactone (I) may be written as a γ-lactone since it gives aqueous solutions with a constant optical rotation. This molecule has three diol bonds that one would expect to be split by periodic acid. These are the primary–secondary, the primary–tertiary, and the secondary–tertiary carbon bonds. Cleavage of the secondary–tertiary carbon bond would be expected to proceed at a slower rate than cleavage of the other bonds. For example Prins and Reichstein (18) have oxidized sterols of type A to sterols of type B in good yields.

$$\underset{\text{Sterol A}}{\text{—}\overset{\overset{\text{OH}}{|}}{\underset{|}{\text{C}}}\text{—CHOH—CH}_2\text{OH}} \xrightarrow[\text{periodic acid}]{\text{1 mole}} \underset{\text{Sterol B}}{\text{—}\underset{|}{\text{C}}\text{OH—CHO}}$$

Furthermore it has been the experience of carbohydrate chemists that carbon-to-carbon bonds in rings (as in glycosides) are split more slowly than bonds in open chains (as in sugar alcohols).

The yield of formaldehyde obtained on treating D-α-fructoheptonic lactone (I) with excess periodic acid shows that both primary alcohol groups can be split off (see Table I). If only one mole of periodic acid is used per mole of I the high yield of formaldehyde (0.93 moles) indicates that this type of splitting is faster than ring cleavage. This may not be generally true for all lactones judging from the results obtained with galactonic and mannonic γ-lactones (Table I) where the rather low yield of formaldehyde suggests that either the ring and

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[2] *National Research Council of Canada Post-doctorate Fellow, 1952–53.*

terminal diol bonds are attacked at about the same rate or else the lactone ring is opened rapidly in about half the molecules prior to oxidation.

We have found that the most rapid reaction during the oxidation of fructoheptonic lactone (I) is the cleavage of the terminal diol bond between the secondary and primary carbons. When an aqueous solution of this lactone was treated with an equimolar amount of periodic acid, 0.93 moles of formaldehyde were liberated (Table I). The acids were removed by an acid absorbing resin

TABLE I
YIELD OF FORMALDEHYDE ON OXIDATION OF LACTONES BY PERIODIC ACID

	Periodic acid (moles/mole of lactone)	Reaction time (hours)	Formaldehyde (moles/mole of lactone)
D-α-Fructoheptonic lactone	1	15	0.93, 0.93
	8	0.25	1.07
	10	15	1.83
D-Mannonic γ-lactone	1	0.25	0.42
	1	1	0.45, 0.34
	10	1	0.80
D-Galactonic γ-lactone	1	1	0.49, 0.52
	10	1	0.98
2-*C*-Hydroxymethyl-D-xylonic lactone	10	3	1.95
	10	15	1.98

to give a solution of the lactone (II). This lactone was a sirup but on forming the sodium salt and replacing the sodium by hydrogen, with an ion exchange resin, the crystalline 4-*C*-hydroxymethyl-L-xyluronic acid (III) was obtained in good yield (68%). The structure of this uronic acid was proved (see Fig. 1) by oxidation to 2-*C*-hydroxymethyl-D-xylaric acid (IV), which was characterized as a crystalline diammonium salt, and also by hydrogenation to 2-*C*-hydroxymethyl-D-xylonic acid, which was isolated as the crystalline lactone (V). A tricarboxylic acid was not obtained on prolonged oxidation of III with nitric acid. This is not surprising since Freudenberg and Blummel (5) had difficulty in obtaining one by nitric acid oxidation of hamamelose.

The uronic acid (III) is shown as an open chain in Fig. 1, since it is not known whether it forms a furanose ring with the tertiary hydroxyl or a pyranose ring with the primary hydroxyl. There are two reasons for believing that a ring is formed; firstly, because the compound shows mutarotation and, secondly, because crystals of the uronic acid are deposited from the sirupy lactone (II), on long standing, thus indicating the acid to be the stable modification. The acid would not be expected to be the stable form unless formation of a glycosidic ring has so changed the shape of the molecule that formation of a lactone ring is no longer possible.

The uronic acid (III) was used as a starting material for the preparation of some other new branched-chain carbohydrates, as shown in Fig. 1. Reduction of the aldehyde group followed by reduction of the acid group gave 2-*C*-hydroxymethyl-D-xylose (VI), a crystalline aldose which gave the alcohol (VII) on further reduction. This aldose formed crystalline hydrazones but not osazones.

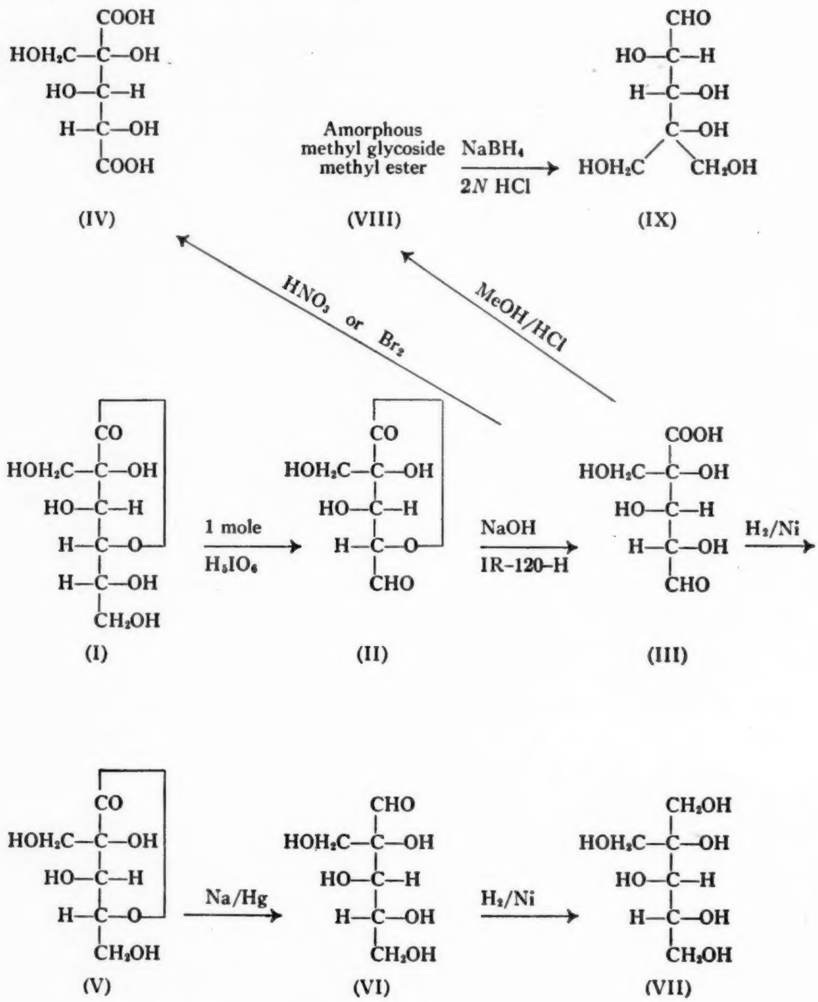

FIG. 1. Branched-chain carbohydrates from D-α-fructoheptonic lactone (I).

Reduction of the carboxyl group (21) of III without reduction of the aldehyde group gave the sirupy 4,4-di(*C*-hydroxymethyl)-D-threose (IX). This aldose was characterized as a crystalline 2,5-dichloro-phenylhydrazone. It also formed an osazone.

The alcohol (VII) was a sirup even after purification as a crystalline hexa-acetate. Its optical rotation, as well as that of fructoheptitol (23), is higher than is usual for unsubstituted pentitols or hexitols. This may be occasioned by distortion of the usual intramolecular arrangement by the side chain (13).

It is difficult to establish the configuration of the asymmetric tertiary carbon in branched-chain carbohydrates since there are no compounds of established configuration to which they can be directly related. The configurations of the branched-chain sugars, apiose (19) and cordycepose (2), were established by applying the empirical acid–salt (15, 16), amide (11, 12), or phenylhydrazide (10, 17) rules to the corresponding aldonic acids and their derivatives. Since the tertiary carbon is not asymmetric in these sugars there is no reason to question the validity of this procedure. Streptose has an asymmetric tertiary carbon but its structure has been fully determined, largely by degradation to compounds of known configuration (3, 8, 22). It was found that dihydrostreptosonic acid obeyed the hydrazide and amide rules (14) thus suggesting that the empirical rules of rotation can be applied to carbohydrates having an asymmetric tertiary carbon atom. Freudenberg *et al.* (6, 7) have concluded that the acid–salt, amide, and phenylhydrazide rules are applicable to α-methyl-α-hydroxy fatty acids.

The rules of rotation have been used by Schmidt and Weber-Molster (20) to assign configurations to three different 2-*C*-hydroxymethyl aldonic acids. They found that hamamelonic acid resembled ribonic acid, D-α-fructoheptonic acid resembled gluconic acid, and D-β-fructoheptonic acid resembled mannonic acid. These acids were thus taken to be the 2-*C*-hydroxymethyl-D-ribonic, 2-*C*-hydroxymethyl-D-gluconic, and 2-*C*-hydroxymethyl-D-mannonic acid, respectively. The configuration assigned to the compounds in this paper is based on Schmidt's formulation of D-α-fructoheptonic acid as 2-*C*-hydroxymethyl-D-gluconic acid. The data on which the assigned configurations are based are collected together in Table II.

TABLE II
SPECIFIC ROTATIONS*

	Free acid	Na salt	Amide	Phenylhydrazide
D-Gluconic acid	−13	+22.5	+61	+35
D-α-Fructoheptonic acid	−45.7	−28.7	−21	+30.5
D-β-Fructoheptonic acid	+ 3.2	+ 5.2	—	−97
D-Mannonic acid	− 2	−19.2	−33.6	−30
D-Ribonic acid	−29.2	+ 4.3	+27.1	+53.8
Hamamelonic acid	−35.6	− 9	—	+97
D-Arabonic acid	+15.8	−11.8 (Calcium salt)	−63.4	−35.6
D-Xylonic acid	− 5	+30.6 (Strontium salt)	+73.5	+50.4
2-*C*-Hydroxymethyl-D-xylonic acid	−57	−34.9	—	—
D-Lyxonic acid	+11	−19	—	−33

* *The rotations tabulated are as given by Schmidt and Weber-Molster (20) except the values for* D-*xylonic and* D-*lyxonic acid which are taken from the current literature and the values for 2-hydroxymethyl-*D-*xylonic acid which are from this paper.*

Schmidt and Weber-Molster were led to the conclusion that the amide and phenylhydrazide rules were applicable to the 2-substituted acids though the acid–salt rule could not be used. We now have the opportunity of applying the latter rule to 2-*C*-hydroxymethyl-D-xylonic acid with the knowledge that the branched-chain acid has the same configuration at carbon-2 as D-α-fructoheptonic

acid. These acids and their derivatives are listed in Table II. The corresponding derivatives of xylose and lyxose are included for comparison. It can be seen that the branched-chain acid derivatives listed obey the empirical rules if the emphasis is altered from the absolute sign of the rotation of the derivatives to the rotations of the derivatives relative to those of the free acids. Thus, if the rules are stated in the form, "the hydroxyl group will be on the right (D) in the normal vertical formula if the salt, amide, and phenylhydrazide are more dextrorotatory, or less levorotatory, than the acid," then the accepted carbon-2 configurations of the acids can be predicted by this generalization. The acid–salt relationship of D-β-fructoheptonic acid is anomalous though the difference between the two rotations is probably not sufficiently great for the rule to be applied with any confidence in this case.

EXPERIMENTAL

General Methods

The micromelting points were determined on a Kofler block and are corrected. Anions and cations were removed from solutions by the weakly basic and strongly acidic Amberlite IR-4B and IR-120 resins respectively, and the filtrates, and other aqueous solutions, were evaporated under reduced pressure in a Craig evaporator (4) (bath temperature about 50–60° C.; 10 mm. pressure). The brucine salts all crystallized with solvent of crystallization, which could not be easily removed. Unless the conditions of drying are specified the physical properties given for these salts are for material dried overnight in a vacuum desiccator containing phosphorus pentoxide and evacuated to about 0.1 mm. The pure salts were crystallized to constant rotation, taken after a standard drying period. Aldose equivalents were determined by oxidation with alkaline iodine as has been used with glucose (9).

Yield of Formaldehyde on Periodic Acid Oxidation of Lactones

Samples of the lactones (1 millimole) were dissolved in water (10 ml.), the solution was cooled in an ice-bath, and the appropriate quantity of 0.1 *M* or 0.5 *M* periodic acid solution added. Excess periodic acid and iodic acid were decomposed with arsenite solution and the formaldehyde was weighed as the dimedone derivative (1). All samples of the formaldehyde-dimedone had m.p. 196 to 198° (uncorr.), undepressed upon admixture with an authentic sample of formaldehyde-dimedone prepared in a similar manner, m.p. 196–197.5° (uncorr.). The results are collected in Table I.

*Preparation of 4-C-Hydroxymethyl-*L*-xyluronic Acid* (III)

A solution of periodic acid (54.8 gm.; H_5IO_6) in water (200 ml.) was added dropwise to a solution of 50 gm. of crystalline D-α-fructoheptonic lactone (23) in 400 ml. of water, the reaction vessel being cooled in an ice–salt bath. After the addition was complete (about 30 min.) the reaction mixture was allowed to stand at 4° overnight and then, while still cold, was passed through a column of Amberlite IR-4B resin sufficient to remove the inorganic acids present (about 350 ml. of resin). The usual precipitation methods of removing the iodic acid were unsatisfactory as traces of this oxidizing acid remained and the hexuronic acid could only be isolated with difficulty and in small yield. Sodium hydroxide

solution (N) was added to the filtrate and washings (about 2500 ml.; pH 3.5) from a Beckman automatic titrator set to maintain the pH at 8.0. About 200 ml. was required over a period of four hours. Cations were removed from the solution by passage through a column of cation-exchange resin and the filtrate evaporated to a sirup which crystallized when diluted with ethanol and seeded with the solid acid prepared as described below. The crystals were filtered off, washed with ethanol, and dried (32 gm.; 68%), $[\alpha]_D^{23.3°}$ $-63.9°$ after two hours (c, 4 in water). Recrystallization from aqueous ethanol gave *4-C-hydroxymethyl-L-xyluronic acid* as short needles, m.p. about 180° (decomp.), $[\alpha]_D^{25.2°}$ $-39.45°$ changing rapidly to $-64.21°$ (c, 1.75 in water). (Found: C, 35.7; H, 5.15; neutralization equivalent, 198.5; aldose equivalent, 189. $C_6H_{10}O_7$ requires C, 37.1; H, 5.2; equivalent weight, 194.)

The mother liquors from which the crystalline acid had separated were neutralized with sodium hydroxide solution, the cations removed, and the theoretical amount of brucine was added. The crude brucine salt (37 gm.; $[\alpha]_D$ -28.6) was recrystallized from aqueous ethanol and dried over calcium chloride in a vacuum desiccator; (21 gm.), m.p. 167–168°, $[\alpha]_D^{26.5°}$ $-25.15°$ (c, 4.7 in water), unchanged by further recrystallization from the same solvent. (Observed constants for the brucine salt of D-α-fructoheptonic acid, m.p. 170°, $[\alpha]_D^{23°}$ $-26.65°$.) Regeneration of the acid from a small portion of the brucine salt gave a sirup which crystallized slowly. The solid crystallized from ethanol as needles, m.p. 130–130.5°, $[\alpha]_D^{22.1°}$ 77.2° (c, 2.0 in water). A specimen of D-α-fructoheptonic lactone had $[\alpha]_D^{23.6°}$ 77.8° and m.p. 130°, unchanged upon admixture with the material just described. The weight of pure brucine salt corresponds to a recovery of 6 gm. of starting lactone, giving an over-all conversion from D-α-fructoheptonic lactone to the crystalline acid of 77%.

Seeds of the crystalline hexuronic acid were first obtained as follows. The calculated amount of brucine was added to a solution of hexuronic acid, free from iodic acid, obtained from 50 gm. D-α-fructoheptonic lactone, and the solution evaporated to a viscous sirup. The brucine salt crystallized when the sirup was diluted with an equal volume of ethanol and cooled. Fractional crystallization of the brucine salt from aqueous ethanol gave three fractions showing constant optical rotation; (a) a brucine salt, probably that of D-α-fructoheptonic acid, (5.5 gm.) $[\alpha]_D^{25°}$ $-27.65°$ (c, 4.2 in water), (b) a salt (20.2 gm.) m.p., after drying over phosphorus pentoxide for seven days, 166–168° (decomp.), $[\alpha]_D^{24.4°}$ $-32.15°$ (c, 4 in water). (Found: C, 57.0; H, 6.35; N, 5.0%), and (c) a salt (73.0 gm.) m.p., after drying over phosphorus pentoxide for five days, 178° (decomp.), $[\alpha]_D^{24.4°}$ $-40.55°$ (c, 4.2 in water). (Found: C, 59.45; H, 5.9; N, 5.05%.) A mixture of equal parts of the salts (b) and (c) melted at 161–165° (decomp.).

Both unidentified brucine salts (m.p. 166–168° and m.p. 178°) yielded crystalline 4-*C*-hydroxymethyl-L-xyluronic acid, which was obtained in 16% and 34% yield (w/w) respectively. The acid from the lower melting salt had m.p. about 180° (decomp.), $[\alpha]_D^{25.2°}$ $-41.2°$ changing to $-64.2°$ (c, 1.7 in water), and the acid from the higher melting salt m.p. 177–180° (decomp.), $[\alpha]_D^{24.4°}$ $-40.2°$ changing to $-65.4°$ (c, 4.2 in water). Both samples of acid gave a brucine salt

m.p. 174° (decomp.), $[\alpha]_D^{24.4°}$ $-40.45°$ (*c*, 4.2 in water.) It seems probable that the lower melting of the two brucine salts was a double salt containing the salt of the hexuronic acid and the salt of D-α-fructoheptonic acid, although this was not verified and only one acid could be isolated from it.

If the crude reaction product, free of inorganic acid, was evaporated, and the neutralization and deionization stages were omitted, a sirup (46.3 gm.; $[\alpha]_D^{24.8°}$ 36.1) was obtained which could not be crystallized, though a sample of the sirup deposited the hexuronic acid described above when left at room temperature for eight weeks. Subsequent neutralization and deionization of the uncrystallizable sirup enabled the crystalline acid to be isolated in the usual yield. Only a single phenylhydrazine condensation product could be isolated from either the sirupy lactone or the crystalline acid. From either material this was obtained from ethanol as yellow, unstable needles, m.p. 160° (decomp.). (Found: C, 57.26; H, 5.85. $C_{18}H_{22}N_4O_5$ requires C, 57.74; H, 5.92.) The product separated in a gelatinous condition and could not be purified satisfactorily.

*Bromine Oxidation of 4-C-Hydroxymethyl-*L*-xyluronic Acid*

The acid (5.0 gm.) was dissolved in water (50 ml.) containing suspended calcium carbonate (30 gm.), the solution cooled to 5°, and bromine (3 ml.) was slowly added with stirring. After standing overnight at 25°, the mixture was filtered and the filtrate concentrated under reduced pressure until free of bromine. The sirup was diluted and filtered through a column of cation exchange resin and again concentrated under reduced pressure, and the sirup was kept at about 40° at 10 mm. for one hour to remove hydrogen bromide in so far as possible. A solution of brucine (30 gm.) in ethanol (100 ml.) was added to the sirup and the solution kept at 4° overnight. The crude salt (37.4 gm.; m.p. 200–205° uncorr.) was dissolved in a minimum of water and the excess brucine removed by extraction with chloroform. The salt crystallized as transparent rectangular plates after the addition of ethanol, (22.1 gm.) m.p. 210° (decomp.). Further recrystallization of a sample gave the pure brucine salt, m.p. 208° (decomp.), $[\alpha]_D^{24.2°}$ $-41.2°$ (*c*, 4.3 in water). Regeneration from the brucine salt (6.5 gm.; m.p. 208° decomp.) gave an acid sirup (1.1 gm.), $[\alpha]_D^{23°}$ $-27.7°$ (*c*, 1.2 in water), which upon treatment with ammonium hydroxide solution gave the crystalline diammonium salt of 2-hydroxymethyl-D-xylaric acid as needles from water and aqueous ethanol, m.p. 146–149° (decomp.), $[\alpha]_D^{23°}$ $-36.1°$ (*c*, 2.1 in water). (Found: C, 29.78; H, 6.63; N, 11.39. $C_6H_{16}O_8N_2$ requires C, 29.51; H, 6.60; N, 11.47%.)

Regeneration from the diammonium salt (1.9 gm.) gave *2-C-hydroxymethyl-*D*-xylaric acid* as a colorless sirup (1.58 gm.), $[\alpha]_D^{25.0}$ -24.88 after five minutes changing to $[\alpha]_D^{23.0}$ $-27.70°$ after 75 hr. (*c*, 2.75 in water). (Found: C, 34.79; H, 4.77; neut. equiv., 106. $C_6H_{10}O_8$ requires C, 34.30; H, 4.80%; neut. equiv., 105.)

*Nitric Acid Oxidation of 4-C-Hydroxymethyl-*L*-xyluronic Acid*

A solution of the uronic acid (7.0 gm.) in water (10 ml.) and nitric acid (10 ml.; specific gravity, 1.4) was kept at 25° for 48 hr. The solution was evaporated under reduced pressure to a thick sirup and the bulk of the nitric acid removed

by repeating the concentration three times after the addition of successive portions of water (100 ml.). Oxalic acid was removed by continuous extraction with ether and the aqueous solution was treated with an excess of brucine; the excess was then removed by extraction with chloroform. The crude brucine salt crystallized when the solution was diluted with ethanol and was recrystallized from aqueous ethanol to give the pure salt as transparent plates (7.75 gm.), m.p. 208° (decomp.), $[\alpha]_D^{23.2}$ −40.7° (*c*, 4.1 in water). Regeneration from a portion of the brucine salt gave a sirup, $[\alpha]_D$ −28.6° (*c*, 7.2 in water) which gave a diammonium salt $[\alpha]_D^{23°}$ −36.65° (*c*, 2.3 in water), m.p. 147–149° (decomp.), which was unchanged upon admixture with the salt obtained from the bromine oxidation described above.

In a subsequent experiment, carried out under identical conditions, the brucine salt obtained had m.p. 170–172°, $[\alpha]_D^{26°}$ −30.6° (*c*, 2.1 in water), and yielded an acid sirup $[\alpha]_D^{23°}$ −8.8° (*c*, 4 in water) which formed an ammonium salt identical with that described above. Oxidation at 60° for 15 hr. gave an acid sirup and diammonium salt identical with those just described.

*2-C-Hydroxymethyl-*D*-xylonic Lactone* (V)

A solution of the crystalline hexuronic acid (15 gm.) in water (50 ml.) was shaken in an atmosphere of hydrogen, in the presence of a Raney nickel catalyst (10 gm. moist solid), at 3700 lb./sq. in., and 100° C. for 12 hr., when it was found to contain less than 5% of the original aldose content. After cooling, the solution was filtered, titrated at pH 7.8 with sodium hydroxide (*N*) solution using a Beckman automatic titrator, and passed through a column of cation exchange resin. The calculated amount of brucine was added and the solution concentrated to a thin sirup which crystallized when diluted with ethanol (2–3 volumes). The crude salt (28.4 gm.) had m.p. 173–174.5°, $[\alpha]_D^{26}$ −27.4° (*c*, 4.2 in water), and was recrystallized once from aqueous ethanol to give the pure salt, m.p. 175°, $[\alpha]_D^{28}$ −28.35° (*c*, 4.2 in water). The acid was regenerated from a solution of the pure brucine salt (25 gm.) in water (75 ml.) by adding sodium hydroxide solution (25 ml.: 2 *N*), filtering off the precipitated brucine, and passing the filtrate through a column of cation exchange resin. After evaporation of the acid solution the crude sirup (9.2 gm.) was heated on the steam bath for two and one half hours, triturated with acetone, and allowed to crystallize. The crude solid (4.75 gm.; m.p. 120–121.2°) was recrystallized from a mixture of ethanol and acetone to give the pure *lactone* as rectangular prisms, m.p. 121°, $[\alpha]_D^{25.5°}$ 107.4° (*c*, 2.2 in water). (Found: C, 40.37; H, 5.95; neutralization equivalent, 179. $C_6H_{10}O_6$ requires C, 40.45; H, 5.66%; neut. equiv., 178.) The product did not reduce alkaline iodine solution. With excess periodic acid 1 mole of the lactone gave 1.95 and 1.98 moles of formaldehyde, determined as the dimedone derivative (see Table I).

The pure lactone gave a brucine salt crystallizing from aqueous ethanol as flat colorless needles, m.p. 175°, $[\alpha]_D^{25}$ −28.41° (*c*, 4.2 in water). (Found: C, 57.6; H, 7.35%.) Addition of the equivalent quantity of standard sodium hydroxide solution to a portion of the lactone gave a solution of sodium 2-*C*-hydroxymethyl-D-xylonate, $[\alpha]_D^{23.5°}$ −16.0° (4.2 in water). Further addition

of the equivalent quantity of standard hydrochloric acid gave a solution containing the free acid, $[\alpha]_D^{23.5°}$ −29.1° changing to −47.4° in 30 days (*c*, 1.8 in water). A sirupy ammonium salt, prepared by adding excess ammonium hydroxide solution to the pure lactone and allowing the solution to evaporate had, after drying over phosphorus pentoxide for 48 hr., $[\alpha]_D^{22.6°}$ −13.85° changing rapidly to −14.25° (*c*, 13 in water). (Found: C, 33.33; H, 7.09. $C_6H_{13}O_6N$ requires C, 33.80, H, 7.09%.)

When the hydrogenation was carried out under milder conditions (2000 lb./sq. in. and 100° C. for two hours) no appreciable reduction occurred and 75% of the starting material could be recovered in the crystalline condition.

*2-C-Hydroxymethyl-*D*-xylose* (VI)

Mother liquors from which crystalline 2-*C*-hydroxymethyl-D-xylonic lactone had been obtained were evaporated and the residue was heated for two hours on the steam bath. The viscous sirup (4.9 gm.) was assumed to be a mixture of the γ and δ lactones since the parent acid had been regenerated from a homogeneous brucine salt. A solution of the sirup in an oxalate buffer solution (4.0 gm. oxalic acid dihydrate in 35 ml. warm water diluted with 16 ml. 2 *N* sodium hydroxide solution) was cooled in an ice-salt bath. Sodium amalgam (89 gm.; 3%) was added portionwise, while the temperature was kept below 10°, and the pH was maintained below 4 by the addition of powdered oxalic acid. After being stirred for a further 45 min., the cold solution was filtered, passed through cation- and anion-ion-exchange resins, and evaporated to a thin sirup. 2,5-Dichlorophenylhydrazine (5.5 gm.) in methanol (30 ml.) was added and the mixture evaporated on the steam bath. The residue set solid on cooling. After washing with ether and water, the crude solid (5.35 gm.; 57%; m.p. 160°) was recrystallized from aqueous ethanol and ethanol to give the pure *2,5-dichlorophenylhydrazone* as colorless plates, m.p. 162–162.5°, $[\alpha]_D^{22.7}$ −9.75° (*c*, 4.1 in pyridine). The magnitude of the rotation fell on standing but the change was accompanied by darkening of the solution so that an equilibrium value could not be obtained. (Found: C, 42.70; H, 4.76; Cl, 20.59. $C_{12}H_{16}O_5N_2Cl_2$ requires C, 42.49; H, 4.76; Cl, 20.91%.)

The sugar did not form an osazone under the usual conditions of osazone formation. A colorless, waxy solid, presumably a phenylhydrazone (cf. Woods and Neish (23)), was obtained from the reaction mixture at one stage, however in the crude state the solid was very unstable and we were not able to isolate any pure material.

The sugar was recovered from the 2,5-dichlorophenylhydrazone (3.0 gm.) after a solution of the derivative in ethanol (25 ml.) and water (37.5 ml.) was refluxed with benzaldehyde (7.5 ml.) and benzoic acid (0.75 gm.), as previously described (23). The resulting sirupy sugar crystallized from an ethanolic solution upon standing for several weeks (1.50 gm.; 94%), m.p. 107–109° (uncorr.), and was recrystallized from ethanol and acetic acid to give the pure sugar as small, colorless needles, m.p. 106–107°, $[\alpha]_D^{24.5°}$ 30.65° after four minutes changing rapidly to 17.45° (*c*, 2.2 in water). (Found: C, 39.93; H, 6.71. $C_6H_{12}O_6$ requires C, 40.0; H, 6.71%.) Aldose equivalent, 182; equivalent wt., 180.

Crystalline 2-*C*-hydroxymethyl-D-xylonic lactone (1.5 gm.; m.p. 120.5–121°) was reduced with sodium amalgam (27 gm.; 3%) as previously described. The sirupy sugar crystallized when triturated with ethanol and seeded with the solid sugar obtained above (0.71 gm.), m.p. 105–106°, unaltered upon admixture with the above sugar (m.p. 106–107°).

1,1-Di(C-hydroxymethyl)-D-threitol Hexaacetate

A solution of crystalline 2-*C*-hydroxymethyl-D-xylose (5.0 gm.) in water (15 ml.) was shaken in an atmosphere of hydrogen, in the presence of a Raney nickel catalyst (1 gm.) until the uptake of hydrogen ceased (four hours), at 2600 lb./sq. in. and 100° C. The catalyst was filtered off and the filtrate concentrated to a sirup (5 gm.) containing 2.4% of unreduced sugar (estimated by hypoidite oxidation).

The bulk of the sirup (4.8 gm.) was acetylated by refluxing with anhydrous sodium acetate (4.7 gm.) and acetic anhydride (60 ml.) for four hours. Isolation of the product in the usual manner gave a gummy acetate which was dissolved in benzene (10 ml.) and filtered through a column of alumina (200 gm.; Merck, washed with 10% acetic acid and then water and dried at 180°). Evaporation of the eluate and washings (1 liter of benzene), which had been collected portionwise, gave fractions all of which crystallized rapidly. The crude fractions (m.p. from 70° to 75° uncorr.) were combined and gave the pure *hexaacetate* (7.4 gm.) as prisms after a single recrystallization from ethanol, m.p. 73°, $[\alpha]_D^{23.0°}$ 27.78° (*c*, 5.3 in chloroform). (Found: C, 49.85; H, 5.97; CH_3CO., 59.0. $C_{18}H_{26}O_{12}$ requires C, 49.77; H, 6.03; CH_3CO., 59.44%.)

The hexaacetate is only weakly adsorbed by the alumina used for removing impurities which hinder the crystallization of the crude acetate. These impurities appear to be strongly adsorbed and to be present in only small amounts so the amount of alumina used above is excessive. Once seeds had been obtained the crude acetate could be crystallized directly.

1,1-Di(C-hydroxymethyl)-D-threitol (VII)

A solution of the pure hexaacetate (3.6 gm.) in anhydrous methanol (15 ml.) and methanolic sodium methoxide solution (0.2 ml.; 2 *N*) was allowed to stand at room temperature for 24 hr. and then evaporated. The sirup was taken up in a little water and extracted with chloroform, then evaporated to give a viscous sirup which was dried over phosphorus pentoxide for 48 hr. (1.8 gm.), $[\alpha]_D^{21.8°}$ −10.2° (*c*, 17.7 in water).

4,4-Di(C-hydroxymethyl)-D-threose 2,5-Dichlorophenylhydrazone

A solution of the 4-*C*-hydroxymethyl-L-xyluronic acid (4.7 gm.) in anhydrous methanol (200 ml.) containing hydrogen chloride (1% w/w) was kept at room temperature for 12 hr., concentrated and the sirup stored in a vacuum desiccator over potassium hydroxide until free of hydrogen chloride (5.1 gm.), $[\alpha]_D^{25.8°}$ −96.5 (*c*, 4.73 in water). The glassy residue (VIII) was dissolved in water (15 ml.) and added dropwise and with stirring to a solution of sodium borohydride (1.0 gm.) in water (20 ml.) during 25 min. The temperature was kept below 40° by the occasional addition of a piece of ice. The stirring was continued for a

further 15 min. and 2 N sulphuric acid was added until the evolution of hydrogen ceased. After standing at 4° for three hours the solution was passed through columns of IR-120 and IR-4B resins and the filtrate evaporated to give a brittle, fluffy solid (3.6 gm.). The solid was heated on the steam bath with dilute hydrochloric acid (36 ml.; 2 N) for two hours and the solution cooled and filtered through a column of IR-4B resin. It was then concentrated to a thin sirup, evaporated on the steam bath with a solution of 2,5-dichlorophenylhydrazine (4 gm.) in methanol (40 ml.), and set aside overnight. The solid which separated was washed with ether and water and crystallized from aqueous ethanol to give the pure *hydrazone* as colorless plates (1.4 gm.), m.p. 137–138°. (Found: C, 42.49; H, 4.76; Cl, 20.60. $C_{12}H_{16}O_5N_2Cl_2$ requires C, 42.49; H, 4.76; Cl, 20.91%.)

4,4-Di(C-hydroxymethyl)-D-*threose* (IX)

A portion of the 2,5-dichlorophenylhydrazone (0.9 gm.; m.p. 137–138°) was treated with benzaldehyde as described above to give the free sugar as a colorless, viscous sirup (0.47 gm.) $[\alpha]_D^{22.6°}$ −60.12° (c, 4.7 in water). Found: aldose equivalent, 204, required 180. From this the rotation of the anhydrous sugar is $[\alpha]_D^{22.6}$ −68.2°. The sugar gave a gelatinous yellow osazone when it was warmed with phenylhydrazine acetate for 15 min. and the resulting solution was cooled; m.p. of the dried material 109–111° (uncorr.).

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THE SILVER CATALYZED OXIDATION OF ETHYLENE

II. KINETICS OF C_2H_4 OXIDATION[1]

By A. Orzechowski[2] and K. E. MacCormack

ABSTRACT

A flow-type apparatus is described and results given for the investigation of the kinetics of the silver catalyzed oxidation of C_2H_4 by oxygen. Using N_2 as diluent, the concentrations of both O_2 and C_2H_4 were varied independently from 9.9 to 79.0% and 2.35 to 9.40% respectively, whilst maintaining a total pressure of 1 atmosphere. Flow rates were varied to give a range of contact times varying from 0.05 to 1 sec. Measurements were made at 234° C. and 274° C. and the data used to estimate initial reaction velocities for both EtO and CO_2 formation as a function of O_2 and C_2H_4 partial pressures. These rates were fitted successfully to equations deduced theoretically in Part IV of the present series.

INTRODUCTION

The development of a catalytic process for the direct oxidation of C_2H_4 to ethylene oxide (EtO) was undertaken in these laboratories several years ago. In spite of the extensive work of Twigg (12) and others it was thus considered important to verify and extend the investigation of the kinetics and proposed mechanism of the reactions concerned. Comprehensive surveys of the work in this field have been presented recently by Pokrovskii (8) and Schultze and Theile (10).

The catalyst developed by Cambron and McKim (3) was used coupled with their principles of reactor design (5) whereby excellent temperature control could be maintained, especially where the highly exothermic CO_2 formation is involved. This catalyst was sufficiently active to permit its convenient adaptation to a flow system with contact times less than one second. Burgoyne and Kapur (2) have reported that EtO undergoes about 30% homogeneous oxidation in one hour at 300° C. It is questionable, therefore, whether static systems involving long contact times can give reliable information for the study of the kinetics of heterogeneous C_2H_4 oxidation.

This paper presents the results of investigations employing wide variations of O_2 and C_2H_4 partial pressures with N_2 as diluent in a flow system maintained throughout at 1 atmosphere. Procedure was adopted according to the findings in Part I of this series, whereby all measurements were made for the catalyst maintained in the same reference state of activity.

APPARATUS

Cylinder gases, O_2, N_2, and C_2H_4 were used throughout with purities specified in Part I. Two-stage reducing valves followed by series needle valves ensured very constant flow rates measured by capillary flow meters carefully calibrated and having an accuracy of ±1%. These could be adjusted and left without attention for periods up to 24 hr.

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The catalyst (3) was prepared by grinding a Ag–Ca alloy containing 8.5 wt. % Ca and pressing the granules (−20 + 100 mesh) on to pure Ag sheets of 1 mm. thickness. The compacted sheets were then steamed for five hours at 350° C. and subsequently boiled for two hours in 20 vol. % aqueous acetic acid.

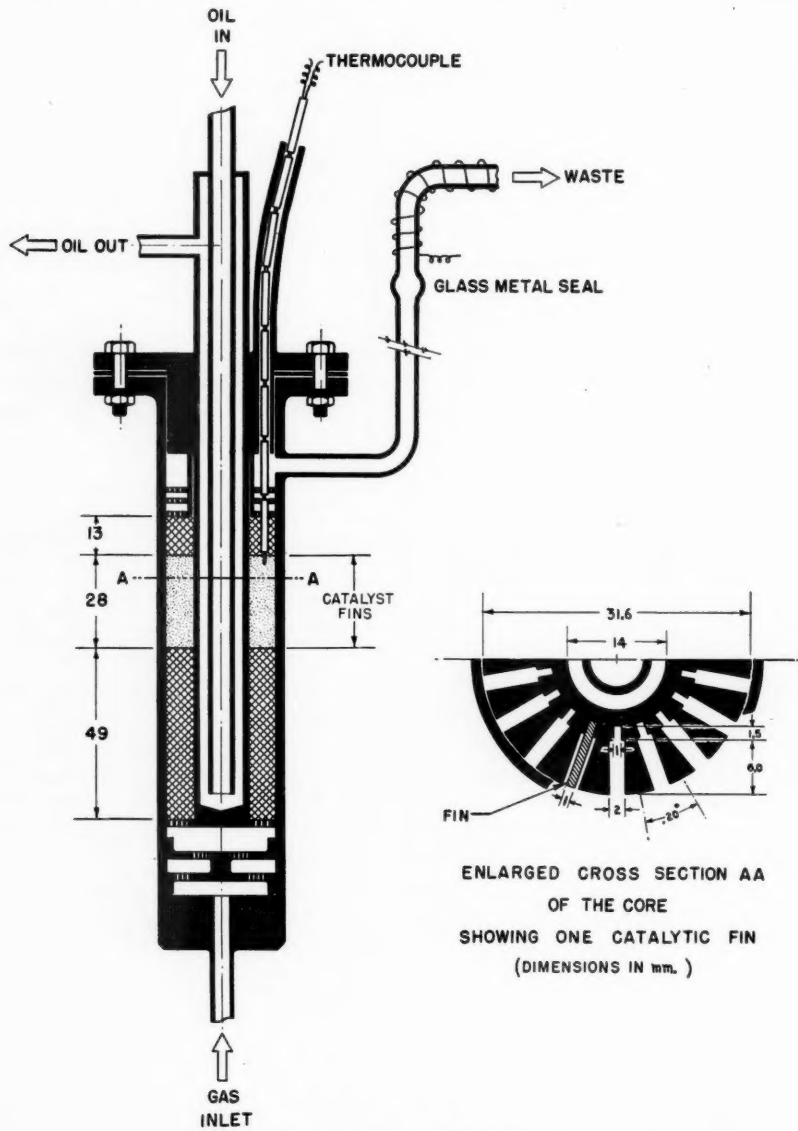

FIG. 1. Diagram of reactor.

By this treatment the Ca content was reduced to 0.48 wt. % to give a highly porous and active catalyst.

The reactor, made of brass and silver plated inside, shown in Fig. 1, consisted essentially of a central core carrying circulating oil as the heat transfer medium and of a shell machined to fit very closely. Catalyst strips or fins are mounted radially in 18 longitudinal grooves cut 0.15 cm. deep in the core surface. Each fin shown as the shaded area in the cross section *A–A* was 2.8 cm. long × 0.75 cm. wide. The free space between each fin was reduced by fillers on the core, shown as the black areas in the cross section *A–A*. The lower and extreme upper portion of the core carried similarly mounted pure Ag fins (cross-shaded area in the side elevation) which served respectively to preheat the reaction mixture and preserve flow symmetry at the end of the catalyst zone. The free cross-sectional area for gas flow comprised 36 rectangular elements each 6.0 × 0.5 mm., equivalent to a total area of 1.1 cm^2. The reaction zone free volume was 3.1 cm^3. Pressure drop through the reactor was negligible at the maximum flow rate of 170 liters/hr., amounting to approximately 8 mm. H_2O. The geometric area of the exposed catalyst surface was 60.5 $cm.^2$, whereas on the basis of B.E.T. area measurements on a similar catalyst sample, the actual area would be approximately six square meters, assuming a total of 12 gm. of granular catalyst compacted on the fins.

One fin was cut near the end, normal to the core axis and the short fin thereby produced was firmly peened into the groove. A chromel–alumel thermocouple was previously silver-soldered to this isolated fin. In this way only a small fraction of the total catalyst was damaged by the heat necessary during soldering. Though the catalyst surface temperature was not measurable, the location of the couple was adequate for the determination of a reference temperature level.

The thermocouple insulated by ceramic sections passed through a long narrow copper tube to a seal of neoprene tubing made leakproof by a strong clamp on the bare thermocouple wires. The reactor and oil lines were grounded and well insulated by a thick layer of magnesia cement.

The rapidly circulating heat transfer oil (total vol. 500 cc.) was pumped and heated externally, partially by intermittent heat input supplied through a Bristol controller, activated by a thermocouple immersed in the oil. The temperature of the catalyst was measured using a Wheelco model 311 potentiometer and recorded continuously. It was maintained constant within ±0.5° C. over periods of 24 hr. without attention.

In the absence of catalyst no reaction products could be found under operating conditions.

The variations of feed flow rate from 10 to 200 liters N.T.P./hour, which were used, corresponded approximately to contact times of 1 to 0.05 sec.; linear velocities, 2.5 to 50 cm./sec.; Reynolds numbers, 1 to 20. The flow was thus always laminar.

Gas Analysis

Fig. 2 shows the assembly used for gas analysis. Samples varying from 70 to 1000 $cm.^3$ were drawn, at a rate slower than the feed flow rate, into the

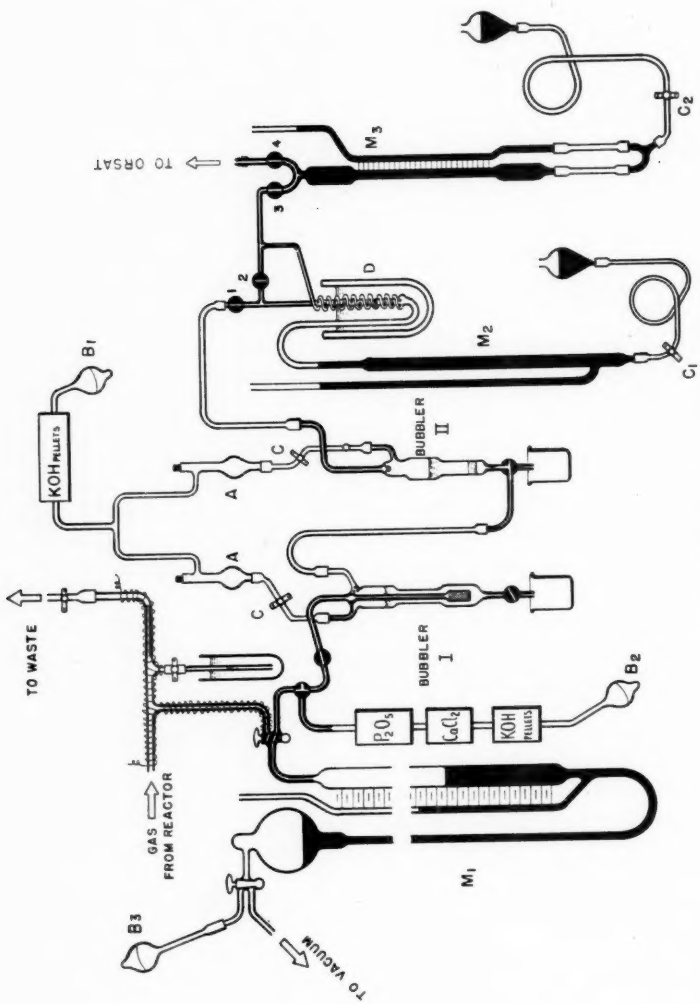

FIG. 2. Gas analysis apparatus.

gas burette, M_1, and, after measuring pressure and temperature the volume was read within 0.5 cm^3. The gas was then forced through the sintered glass bubblers I and II connected in series. Sintered glass was of coarse grade giving very numerous and fine bubbles. Bubbler I contained 10 cc. of 0.05 *N* HCl–$MgCl_2$ solution (1, 4, 6) for EtO absorption, while II contained 5 cc. of 0.1 *N* NaOH for CO_2 absorption. These solutions were pipetted into *A* and forced in by air from rubber bulb B_1.

After gas absorption the excess reagent was back-titrated with reagents of appropriate normality contained in microburettes.

It was shown during blank tests on mixtures of known composition within the experimental range that the II bubbler was efficient for complete absorption of CO_2, that no acid vapors were carried on from I to II, but approximately 2% of EtO could escape absorption in 0.05 *N* HCl–$MgCl_2$ reagent, with a maximum 3% of CO_2 being lost by solution in I, especially with this low concentration of reagent used. In spite of this systematic error, it was essential to the maintenance of accuracy at low conversions to employ this low reagent concentration. No correction was applied for this systematic error.

Gas lines were purged by means of air from the rubber bulb B_2 and thorough rinsing was carried out via *A–A* aided by an air stream from B_1 and B_2. In the case of simultaneous C_2H_4 determination following the bubblers the remaining gas passed through a trap, *D*, immersed in liquid O_2 where C_2H_4 was retained in a small volume of about 10 cc. The content of this trap was subsequently quantitatively transferred by mercury from M_2 (returned by siphoning) to the gas burette M_3 and thence to a Burwell-Orsat type apparatus for C_2H_4 determination. The efficiency of this procedure was tested using samples containing 1–4% C_2H_4 in N_2 which showed that at least 96% of the C_2H_4 could be determined.

The outgas from the reactor was mildly heated to avoid condensation prior to sampling.

In the case of gas samples containing H_2O in excess of the saturation value at room temperature, a correction was applied to the measured volume to

TABLE I
MATERIAL BALANCE BY ANALYSIS

% C_2H_4 converted		% C_2H_4 unconverted	Total %	Deviation from 100%
To EtO	To CO_2			
26.5_5	16.4_5	51.6	94.5	−5.5
40.2	32.1	26.6	98.9	−1.1
11.5_5	13.6_5	68.8	94.0	−6.0
11.5_5	13.5	71.0	96.0	−4.0
16.3	20.3	62.2	98.8	−1.2
16.3_5	19.2	63.1	98.6_5	-1.3_5
17.7	19.3_5	57.8	94.8_5	-5.1_5
17.7_5	22.9	55.7	96.3_5	-3.6_5
17.7	22.8	56.2	96.7	−3.3
15.2_5	27.1	55.0	97.3_5	-2.6_5
32.1	35.9	32.6	100.6	+0.6
			Mean deviation	−3.0

allow for the water condensed in the sampling burette. Dry air was added after volumetric measurements were complete, to vaporize the condensate which could retain some ethylene oxide. Since the amount of H_2O is equivalent to the CO_2 produced, the former is accurately known for correction purposes.

Table I indicates the accuracy with which complete determination of the reaction products could be achieved. The mean deviation of -3% from the ideal 100% appears to indicate a systematic error very likely attributable to the incomplete absorption of EtO and C_2H_4 in the reagents used and the probable loss of some CO_2 in bubbler I.

Gas flow rates and titration procedure are each accurate within $\pm 1\%$. Accordingly, the expected accidental error in the final C_2H_4 conversion values is approximately $\pm 2\%$ of the absolute values.

RESULTS

C_2H_4 oxidation was investigated at 274° C. and 234° C., two or three measurements being made after a period of constant operating conditions lasting approximately 24 hr. Reproducibility was within the limits of the foregoing estimated accuracy as is illustrated in Figs. 1 and 2, Part I. The rapid equilibria referred to in Part I were well established in this time with no significant onset of interference by slow processes within the range of composition studied. The latter processes are less significant with decreasing temperature, but may become appreciable when oxygen deficient mixtures are used.

The composition of the gas mixture entering the reactor and its flow rate are expressed by symbols pE_nO_m, where p refers to the flow rate, n to C_2H_4 partial pressure, m to oxygen partial pressure.

Chosen purely for convenience, the unit of total flow rate p is 41.8 liters N.T.P./hour, the unit of ethylene partial pressure n is 17.9 mm. Hg, the unit of oxygen partial pressure m is 75 mm. Hg.

The catalyst quantity, constant throughout, is taken as unity.

The reaction time co-ordinate is defined as: catalyst quantity/gas mixture feed flow rate. For example, $0.5E_2O_2$ refers to a feed flow rate of 20.9 liters N.T.P./hour, the partial pressures in the feed, at total pressure of 1 atm. being C_2H_4, 35.8 mm. Hg; O_2, 150 mm. Hg; the remainder, N_2 and the reaction time co-ordinate is 2.0.

1. Runs at 274° C.

Preliminary conditioning had been carried out at 234° C. along with an investigation of the slow processes described in Part I. At 274° C. treatment involving the standard check run ($1E_2O_2$) approximating a 20:1 air–C_2H_4 mixture, was followed by the kinetic series lasting about 900 hr. The dependence of C_2H_4 conversion on flow rate and partial pressures of C_2H_4 and O_2 are shown in Table II.

All the data are corrected to the reference state finally established at the end of the series (run 49) by the procedure described later. Experimental values measured for the check run conditions at various times through the series are given at the end of this table and indicate a slight decline in total catalyst activity up to run 26.

TABLE II
CONVERSION OF C_2H_4 AT 274° C.
(TOTAL PRESSURE = 1 ATM.)

Run No.	Feed composition symbol	Reaction time co-ordinate	% C_2H_4 converted to: C_2H_4O	% C_2H_4 converted to: CO_2	Selectivity, %	% O_2 converted Total
5	E_2O_2	0.25	17.0	15.2	52.8	12.78
3	"	0.50	26.4	24.3	52.0	20.47
1	"	*1.00*	35.6	33.9	51.3	28.36
2	"	2.00	40.5	41.0	49.1	34.21
4	"	4.00	39.0	49.0	44.3	39.76
11	E_2O_4	0.167	15.4	14.4	51.7	6.07
13	"	0.25	20.0	19.0	51.3	7.99
9	"	0.50	29.0	28.2	50.6	11.81
7, 10	"	*1.00*	38.5	37.5	50.6	15.70
8	"	2.00	41.0	46.6	46.8	19.10
12	"	4.00	38.0	52.5	42.0	21.05
17	E_4O_2	0.25	11.4	10.5	52.0	17.7
15	"	0.50	18.6	17.0	52.2	28.7
14, 18	"	1.00	27.6	26.0	51.5	43.8
16	"	2.00	35.0	33.5	51.0	56.2
19	"	4.00	35.0	39.0	47.2	64.0
24	E_4O_4	0.25	16.0	14.5	52.5	12.29
21	"	0.50	23.6	22.2	51.5	18.72
23	"	*1.00*	32.2	31.0	50.9	26.05
22	"	2.00	38.0	38.5	49.7	32.14
25	"	4.00	38.4	46.4	45.3	37.79
29	E_1O_1	0.20	16.8	15.7	51.7	13.26
27	"	0.50	28.5	27.1	51.1	22.89
28	"	*1.00*	35.6	35.8	49.7	29.91
30	E_1O_1	2.00	37.7	42.1	47.1	34.70
31	"	4.00	31.5	48.4	39.4	38.47
37	E_1O_4	0.125	14.0	14.0	50.0	2.92
36	"	0.250	23.0	23.0	50.0	4.80
32	"	0.50	31.0	32.5	48.8	6.74
33	"	*1.00*	37.2	42.5	46.7	8.71
34	"	2.00	35.0	51.[illegible]	40.4	10.26
35	"	4.00	28.5	58.0	32.9	11.23
38	E_4O_1	0.167	5.8	5.9	49.6	19.66
39	"	0.250	7.8	8.0	49.3	26.60
40	"	0.50	12.5	12.8	49.4	42.61
41	"	*1.00*	16.6	18.8	46.8	61.71
42	"	2.00	17.2	22.3	43.5	72.00
43	"	4.00	14.0	25.8	35.2	80.47
Checks of standard run—E_2O_2						
6	E_2O_2	1.00	38.0	35.0	52.0	After E_2O_2
20	"	1.00	36.8	36.0	50.5	After E_4O_2
26	"	1.00	36.7	33.0	52.6	After E_4O_4
44	"	1.00	32.8	35.9	47.8	After E_4O_1
47	"	1.00	33.5	35.0	49.0	After E_4O_1
48	"	1.00	35.3	34.4	50.7	After E_4O_1
49	"	1.00	35.6	33.9	51.3	After E_4O_1

The final kinetic runs 38–43, using the composition E_4O_1, resulted in almost permanent decrease of selectivity* indicated by check run 44. (Twofold and

* *Selectivity = % C_2H_4 converted to EtO/total % C_2H_4 converted.*

sixfold increase in flow rate using standard E_2O_2 feed gave similarly abnormal selectivity at this moment: runs 45 and 46 (not shown).)

Attempts were made to restore the original standard selectivity following E_4O_1 runs. Fifty hours operation at $1E_2O_2$ (274° C.) showed slight improvement (run 47) but equally effective was a six hour pretreatment by air (274° C.)—run 48, and further 50 hr. of operation at $1E_2O_2$ (run 49).

For the purpose of studying the kinetics, some reference state for the surface had to be chosen. It should be recalled that the initial and final check runs (run 6 and 49) do not differ much respecting selectivity; on the other hand the total activity declines up to check run 26 and then remains constant; this is most likely attributable to slight over-all sintering of the surface during the first kinetic runs, with subsequent stabilization of the catalyst. Therefore the apparently more stable final state (run 49) was chosen as the reference state for the surface and all experimental values were then corrected on the basis of the relation between this final standard run and the check runs made immediately following each composition group.

Figs. 3 and 4 show C_2H_4 conversions to EtO and CO_2 respectively as a function of the reaction time co-ordinate defined above.

Several analyses for acetaldehyde in the products were made, especially during the runs for E_4O_1, which are likely to constitute the most favorable conditions for its formation; none was ever detected though the method (see Part III) was checked for its sensitivity to quantities which would account for 0.1% conversion of C_2H_4 to acetaldehyde.

2. Runs at 234° C.

A further conditioning period at 234° C. with the standard flow rate and composition ($1E_2O_2$) followed the kinetic series at 274° C. Measurements were made over a period of 100 hr. to ensure that a steady state had been

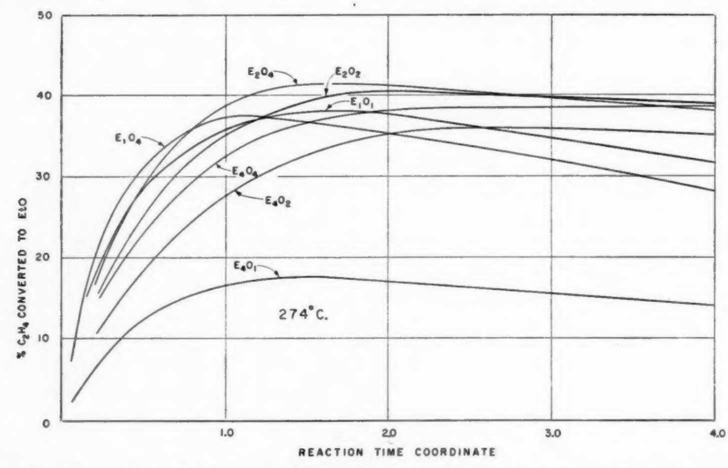

FIG. 3. Conversion of C_2H_4 to EtO at 274° C. vs. reaction time for different feed compositions.

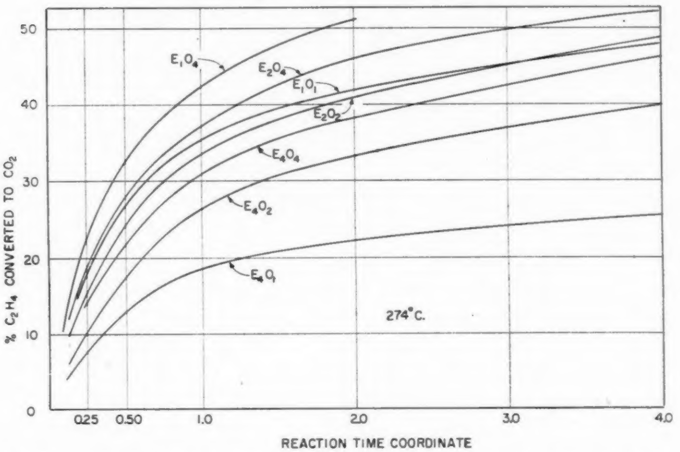

FIG. 4. Conversion of C_2H_4 to CO_2 and H_2O at 274° C. vs. reaction time for different feed compositions.

achieved. The experimental results measured at 234° C. over a total period of approximately 1200 hr. are presented in Table III and plotted in Figs. 5 and 6.

Frequent checks of the reference conditions are included in this table and indicate no departure from the standard state until the oxygen-deficient runs E_4O_1 were made. All subsequent check runs were indicative in general of higher conversion to CO_2 and lower conversion to EtO than were the previous standards. This behavior is similar to that observed at 274° C. and again responded slightly to oxygen treatment (cf. runs 19 and 18). Further recovery was effected by operating with composition E_1O_8 (check run 23). Prolonged operation under standard conditions following E_4O_8 runs effected some restoration of selectivity (cf. runs 27 and 28). The standard reference state of the catalyst adopted here is that of run No. 13.

3. Corrections of Results for Changed Reference State

(*a*) *Corrections at 274° C.*

The experimental conversions E_2O_2 established during runs 1–5 were plotted against reaction time co-ordinate. The conversions of $1E_2O_2$ chosen as reference state (run 49) corresponded on this plot to a reaction time co-ordinate only about 0.8 instead of 1. Therefore it was assumed that about 20% of the surface was lost by sintering during the kinetic series, and the reference plot E_2O_2 for the final state of the surface, corresponding to run 49 was established by increasing the reaction time co-ordinate of the experimental conversions in runs 1–5 by a factor of 1/0.8.

In this way the corrected conversions of E_2O_2 (runs 1–5 in Table II) were obtained and were considered to be the reference plot for the other check runs.

Subsequently the other results were corrected by comparing the conversions of check runs made after each composition group with this reference plot

TABLE III
CONVERSION OF C_2H_4 AT 234° C.
(TOTAL PRESSURE = 1 ATM.)

Run No.	Feed composition symbol	Reaction time co-ordinate	% C_2H_4 converted to: C_2H_4O	CO_2	Selectivity, %	Checks *
A. Experimental values						
1	E_4O_4	0.25	5.02	3.36	60.0	
2	"	0.50	8.35	5.26	61.2	
3	"	1.00	14.35	8.35	63.2	
4	"	0.25	5.29	3.36	61.2	
5	E_2O_2	1.00	17.60	10.52	62.6	*
6	E_1O_1	1.00	17.60	11.05	61.5	
7	"	0.50	12.20	8.15	60.0	
8	"	1.00	17.70	11.00	61.6	
9	E_2O_2	1.00	17.05	10.52	61.9	*
10	E_1O_4	1.00	27.80	16.85	62.2	
11	"	0.50	18.62	11.20	62.5	
12	"	0.25	10.70	6.33	62.9	
13	E_2O_2	1.00	16.95	10.50	61.7	*
14	"	0.50	10.80	7.10	60.2	
15	"	0.25	6.73	4.92	57.8	
16	E_4O_1	1.00	6.32	5.29	54.5	
17	"	0.50	3.70	3.50	51.4	
18	E_2O_2	1.00	14.00	12.20	53.5	*
19	E_2O_2	1.00	16.70	12.80	56.6	*
20	E_1O_8	0.50	20.10	13.65	59.6	
21	"	0.25	11.80	8.90	57.0	
22	E_1O_8	1.00	28.63	17.70	61.90	
23	E_2O_2	1.00	16.90	11.80	58.9	*
24	E_4O_8	1.00	16.50	11.30	59.4	
25	"	0.25	6.50	4.70	58.1	
26	"	0.50	11.05	7.76	58.9	
27	E_2O_2	1.00	17.20	13.15	56.7	*
28	"	1.00	16.10	11.50	58.4	*
B. Experimental values corrected						
16	E_4O_1	0.50	4.9	3.0	62	
17	"	0.25	2.7	1.8	60	
20	E_1O_8	0.50	20.10	11.7	63	
21	"	0.25	11.80	7.2	62	
25	E_4O_8	0.25	6.50	3.6	64	
26	"	0.50	11.05	6.1	64	

above. For instance the check run 44 following the composition group E_4O_1 shows a change in conversions relative to the reference plot of E_2O_2 corre-

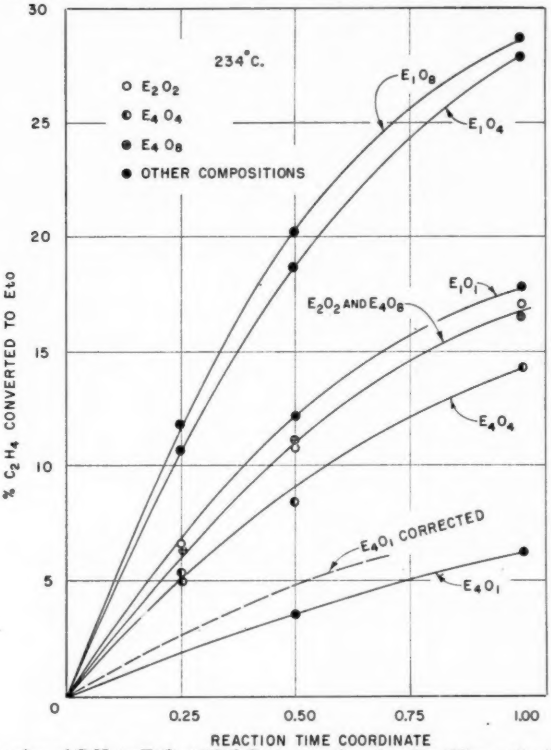

FIG. 5. Conversion of C_2H_4 to EtO at 234° C. vs. reaction time for different feed compositions.

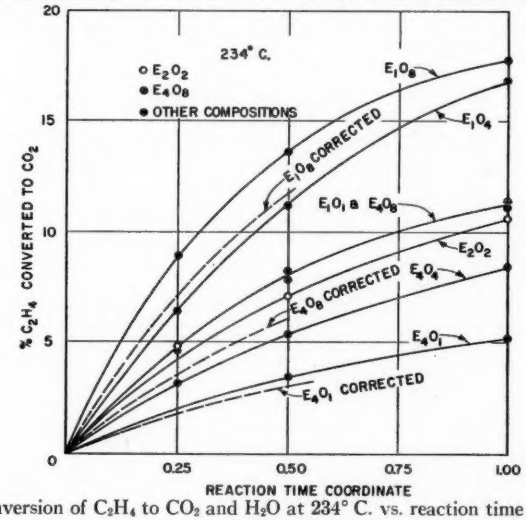

FIG. 6. Conversion of C_2H_4 to CO_2 and H_2O at 234° C. vs. reaction time for different feed compositions.

sponding approximately to a 10% increase in reaction time respecting CO_2 and a 10% decrease in reaction time respecting EtO. The catalyst behaves as if its surface had been increased for CO_2 production and decreased for EtO production.

The correction procedure applied to the E_4O_1 group therefore involved correction of the reaction time co-ordinate by a factor which increased it respecting CO_2 production and decreased it respecting EtO production, the magnitude of the factor being determined by the relative increase and decrease of the time co-ordinates for the standard check conversions immediately following these runs.

(*b*) *Corrections at 234° C.*

Since no sintering was observed, the reference plot for the standard E_2O_2 composition versus reaction time co-ordinate was chosen using the experimentally observed conversions (runs 13–15). Corrections similar to those explained for run E_4O_1 at 274° C. were applied here to the data on compositions: E_4O_1, E_1O_8, and E_4O_8, since these were investigated during or after the irreparable inhibition caused by composition E_4O_1.

4. Initial Reaction Rates

The rate of reaction may be calculated at a given contact time from the plots of C_2H_4 conversion versus reaction time co-ordinate. This rate, r, is expressed by the relation,

$$r = dx/d\frac{M}{F_E} = V_E\,dx/d\frac{M}{F} \tag{1}$$

where

x = fractional C_2H_4 conversion to a given product,
M = catalyst amount (constant throughout; assumed unity as described earlier),
F_E = C_2H_4 feed flow rate (arbitrary units described previously),
F = mixture feed flow rate in the same units,
V_E = vol. or mole fraction of C_2H_4 in feed mixture.

TABLE IV
INITIAL RATE (r_0) OF ETHYLENE OXIDE FORMATION

Feed composition symbol	Feed gas volume fraction		$\left[dx/d\frac{M}{F}\right]_0^*$		$r_0 = \left[dx/d\frac{M}{F}\right]_0 V_E$ *			
					234° C.		274° C.	
	V_E	V_O	234° C.	274° C.	Exp.	Calc.	Exp.	Calc.
E_1O_1	0.0235	0.0988	0.30	0.95	0.00706	0.0072	0.0223	0.0229
E_1O_4	0.0235	0.395	0.46	1.25	0.0108	0.0112	0.0294	0.0307
E_1O_8	0.0235	0.790	0.54	—	0.0127	0.0124	—	0.0326
E_2O_2	0.0471	0.198	0.26	0.87	0.0122	0.0125	0.0410	0.0411
E_2O_4	0.0471	0.395	—	1.02	—	0.0158	0.0476	0.0486
E_4O_1	0.0942	0.0988	0.11	0.40	0.0103	0.0100	0.0377	0.0387
E_4O_2	0.0942	0.198	—	0.55	—	0.0150	0.0518	0.0543
E_4O_4	0.0942	0.395	0.21	0.74	0.0198	0.0199	0.0697	0.0682
E_4O_8	0.0942	0.790	0.26	—	0.0245	0.0238	—	0.0784

* *The arbitrary unit used is: 41.8 liters (N.T.P.)/hour for the constant amount of catalyst used.*

The rate, r, is thus expressed in the arbitrary units of 41.8 liters (N.T.P.) of product per hour for the constant amount of catalyst employed. The initial reaction rates, r_0, have been obtained by extrapolation of the data to zero conversion and time; for EtO formation these are presented in Table IV. Initial rates of reaction may be simply expressed in terms of the partial pressures of C_2H_4 and O_2 only, since reaction products may be assumed absent at this stage. The results could not be fitted to an equation of the type,

$$r_0 = kp_E^a\, p_O^b$$

nor in general to the equation,

$$r_0 = k.f(p_E).f'(p_O)$$

where f is a function only of p_E, and f' a function only of p_O.

In Part IV which deals with the proposed reaction mechanism, reasons will be given which led, on the basis of the known adsorption behavior of O_2 and

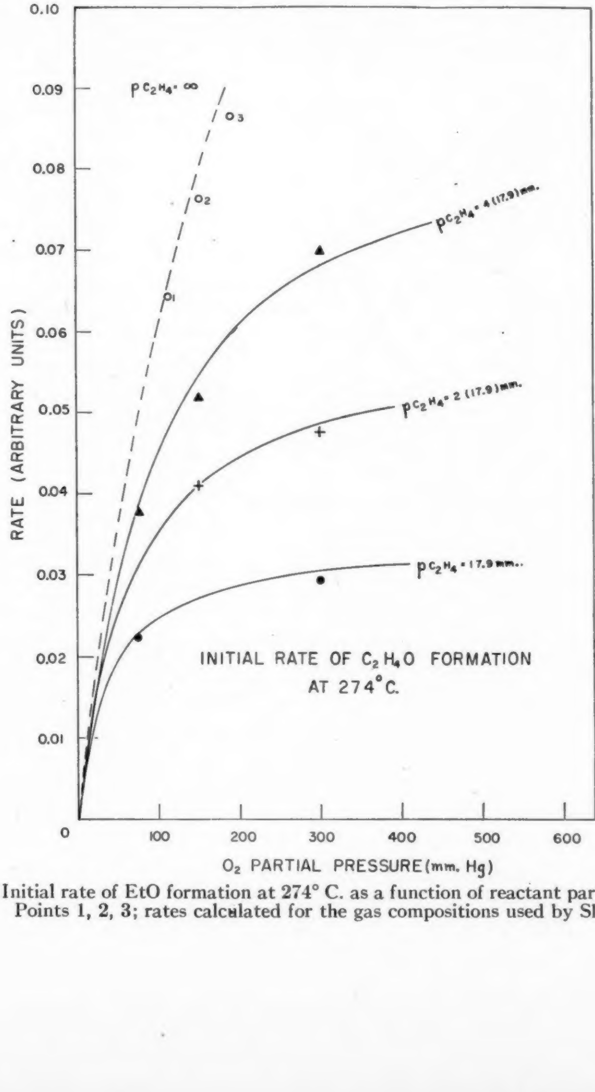

FIG. 7. Initial rate of EtO formation at 274° C. as a function of reactant partial pressures. Points 1, 2, 3; rates calculated for the gas compositions used by Shen-Wu Wan.

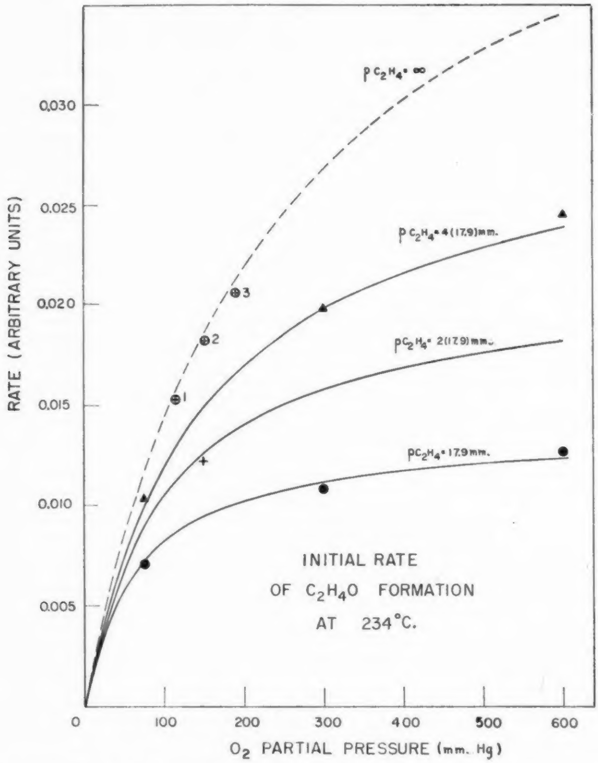

FIG. 8. Initial rate of EtO formation at 234° C. as a function of reactant partial pressures. Points 1, 2, 3; rates calculated for the gas compositions used by Shen-Wu Wan.

C_2H_4 to the development of a rate equation of the type,

$$r_0 = \frac{k}{1 + \dfrac{a}{p_E} + \dfrac{b}{p_O}}. \tag{2}$$

The constants were calculated from the experimental data for EtO formation by the method of least mean squares. With r_0 expressed in the above units and partial pressures in mm. of Hg, these are as follows:

Temperature	k	a	b
274° C.	0.200	86	225
234° C.	0.048	45	240

The applicability of these equations over the whole range of pressures employed may be judged by the close agreement between experimental and calculated values of the rate shown in Table IV, and in Figs. 7 and 8. The solid lines of the latter are calculated according to these equations.

TABLE V

COMPARISON OF SHEN-WU WAN EXPERIMENTAL DATA WITH VALUES OBTAINED USING THE PROPOSED EQUATION FOR THE REACTION VELOCITY

Temp.	Feed composition, vol. %		Partial pressures feed gas, mm. Hg		Shen-Wu Wan: Initial rate (R) EtO formation (gm. mol./hr. gm. catalyst)	Rate (r) calc. for N.R.C. reactor (units of this paper*)		r/R
	C_2H_4	O_2	C_2H_4	O_2				
230° C.	85	15	645	114	0.00127	0.0152	(a)	11.95
	80	20	607	152	0.00151	0.0182		12.03
	75	25	570	190	0.00171	0.0206		12.03
260° C.	85	15	645	114	0.00386	0.0646	(b)	16.75
	80	20	607	152	0.00457	0.0765		16.75
	75	25	570	190	0.00518	0.0865		16.70

* *The unit is: 41.8 liters (N.T.P.)/hour for the constant amount of catalyst used in N.R.C. reactor.*

(*a*) *Calculated for 234° C.*

(*b*) *Calculated for 274° C.*

Substantial confirmation of the form of the equation is provided by the data of Shen-Wu Wan (9). These data include C_2H_4 concentrations higher than those employed in this work by a factor of about ten. Table V presents a comparison of the rate of EtO formation calculated on the basis of the above equation with the rates measured by Shen-Wu Wan. Since it would be unlikely that similar activity per unit mass of Ag exists in each work, no attempt to convert to similar rate units is made. However, the ratio of the rates should be constant, as was found to be the case. The numerical difference between the two sets of ratio values given in Table V arises because ratio (*a*) involves Shen-Wu Wan's data at 230° C. and present data at 234° C., and ratio (*b*) involves comparison of the respective data at 260° C. and 274° C.

The constant k is very temperature sensitive but the form of the dependence is not definitely known. It can be shown, however, assuming that ln k is proportional to reciprocal absolute temperature, that isothermal rate ratios are constant and independent of temperature. Since the constants a and b are not very dependent on temperature this procedure is justified.

Figs. 7 and 8 include the rates calculated for the present reactor for feed compositions employed by Shen-Wu Wan (points 1, 2, and 3) and the limiting curve (broken line) for infinite C_2H_4 partial pressure. Similar qualitative curves are obviously obtained for rates plotted as a function of C_2H_4 partial pressure with O_2 pressure constant.

DISCUSSION

In general it may be concluded that the present work confirms the observations made by Twigg (12) that there are two main simultaneous reactions, namely, C_2H_4 oxidation to EtO and also to CO_2 and H_2O and, in addition, a consecutive reaction for EtO oxidation. The maximum occurring in the con-

version to EtO arises when the rate of EtO formation becomes equal to its rate of oxidation. The data do not support the belief expressed recently (11), and kindly drawn to our attention by Dr. N. Thon, that all CO_2 is formed by consecutive oxidation of EtO. Selectivity at zero conversion appears to approach values appreciably different from 100%, the latter being of necessity expected if the initial rate of CO_2 formation approached zero. Observed values lie between 50–52% at 274° C. and 60–64% at 234° C. Furthermore, the rate of EtO oxidation, reported in Part III, was found too low to account for all the CO_2 produced during C_2H_4 oxidation. It is also noteworthy that the data of Shen-Wu Wan (9) at extremely low C_2H_4 conversion (0.2 to 2%) indicates a constant selectivity of about 60%.

In contrast to the data reported by Twigg (12) C_2H_4 conversion to CO_2 was not approximately linear with time. In consequence, selectivity did not vary greatly with reaction time up to the maximum in conversion to EtO. As mentioned earlier declining selectivity could be due to homogeneous EtO oxidation (2) likely to occur under static conditions where reaction times of several minutes rather than fractions of a second are used. It will be noted also that selectivity at zero conversion or time appears to be independent of the reactant composition. This leads to the conclusion that each of the parallel reactions is initiated by the same kind of reaction step with similar rate dependence on reactant concentrations. The initial rates of formation of CO_2 can be shown to be about 95% and 60% of the rates of EtO formation at 274° C. and 234° C., respectively.

No attempt has been made at this stage to interpret the rapidly declining rate with increasing time on a basis such as inhibition by reaction products. The primary object of this work has been to provide information concerning the reaction mechanism which will be described in Part IV.

The present results are consistent with those of Murray (7) respecting the influence of reactant partial pressures. With respect to the influence of total pressure, reference to Fig. 7 of that publication shows similar qualitative trends to those observed at reaction time co-ordinate 2 for runs E_1O_1, E_2O_2, and E_4O_4 where the total pressure of the reactants varies as 1:2:4.

The present investigation may also be of value in determining optimum operating conditions for the production of EtO by direct oxidation of C_2H_4. The following summary shows the influence of conditions on reaction behavior at 274° C.

I. Influence of p_{O_2}, at constant $p_{C_2H_4}$

(*a*) Low $p_{C_2H_4}$

High rate of conversion, increasing with p_{O_2}. The maximum conversion to EtO is obtained more rapidly with increasing p_{O_2}. However, large O_2 excess can possibly result in a slight decrease of the maximum EtO value, by virtue of increased EtO combustion.

(*b*) High $p_{C_2H_4}$

Low rate of conversion and low maximum conversion to EtO both increasing at first largely, then more slowly, with increasing p_{O_2}. However, the maximum is attained at shorter contact time with decreasing p_{O_2}.

II. Influence of $p_{C_2H_4}$ at constant p_{O_2}

(*a*) Low p_{O_2}

Large decrease of conversion rate and of the value of the EtO maximum with increasing $p_{C_2H_4}$. The time required to attain maximum conversion to EtO does not seem to vary.

(*b*) High p_{O_2}

Decrease of conversion rate and increase of the time required to attain maximum conversion to EtO with increasing $p_{C_2H_4}$. The value of the EtO maximum increases with $p_{C_2H_4}$, at least within a certain range.

III. Influence of total pressure; $p_{O_2}/p_{C_2H_4}$ = const.

The conversion rate decreases and the time required to attain maximum conversion to EtO increases slightly with total pressure. However, the value of the EtO maximum increases with pressure at least within a certain range.

By virtue of this complex behavior it cannot be said definitely that high p_{O_2} and low $p_{C_2H_4}$ are to be chosen for optimum EtO production. For instance, a high EtO maximum can be obtained relatively quickly with the feed E_2O_4, where C_2H_4 content was average respecting the range investigated.

The proposed reaction mechanism will be presented in a later publication (Part IV) where the present results will be compared with those on EtO oxidation.

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THE SILVER CATALYZED OXIDATION OF ETHYLENE

III. KINETICS OF ETHYLENE OXIDE OXIDATION[1]

By A. Orzechowski[2] and K. E. MacCormack

ABSTRACT

A flow type apparatus was used for kinetic studies of the silver catalyzed oxidation of ethylene oxide (EtO) by oxygen at 274°C. Using N_2 as diluent the concentrations of O_2 and ethylene oxide were varied independently from 9.9 to 79% and 2.35 to 9.4% respectively while a total pressure of 1 atmosphere was maintained. Flow rates were varied to give a range of contact times varying from 0.06 to 0.25 sec. It was shown that EtO is oxidized without previous dissociation into C_2H_4 and O_2. The dependence of the initial rate of oxidation of EtO on reactant concentrations excludes isomerization of EtO (to acetaldehyde) as a main step in its oxidation, and a direct oxidation mechanism is suggested. The results of a few experiments to determine the extent of isomerization of EtO to acetaldehyde in the absence of oxygen are presented. No steady state could be achieved but the results may be used semiquantitatively to support the belief that isomerization is not the rate determining step in the oxidation of ethylene oxide.

INTRODUCTION

In order to further the establishment of a reaction mechanism for the oxidation of C_2H_4 on a silver catalyst, Parts I and II of this series are here supplemented by a study of the oxidation of ethylene oxide (EtO) and its isomerization on the same catalyst sample.

EXPERIMENTAL

The apparatus, catalyst sample, and determination of reaction products have been described in Part II. The source of the gases used and their purity was specified in Part I.

Flow rates of EtO were controlled by a two-stage reducing valve followed by three needle valves in series. Mild infrared heating of the cylinder head and reducer ensured constancy of flow with downstream pressure of about 7 P.S.I.G. A dual range orifice meter was used (1–5 and 5–20 liters/hr.) filled with Apiezon-B oil, and having a scale graduation accurate to 0.5%. This was calibrated by mixing the EtO with a N_2 stream of known flow rate to cover a range of composition from 1.5 to 10% EtO. Samples were drawn into a gas burette and the EtO content determined within 1% of the true value employing previously described techniques.

To determine acetaldehyde samples were measured into a mercury burette and then forced through a sintered glass bubbler containing a solution of hydroxylamine hydrochloride.* The HCl liberated by the equivalent amount of aldehyde was titrated with NaOH from microburettes. Checks on the efficiency of this method were made by vaporizing pure liquid acetaldehyde

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**Seven grams of $NH_2OH.HCl$ was dissolved in 100 cc. of water. For each determination 0.1 cc. of this reagent was diluted with 10 cc. H_2O, a drop of bromophenol blue solution added, and titrated with 0.005 N NaOH to the first blue color, before absorption of aldehyde.*

into a mercury burette. After measuring the pressure, volume, and temperature of the sample, N_2 was added to give 0.1% CH_3CHO by volume. The estimation of hydroxylamine hydrochloride accounted for at least 75% of the aldehyde present.

Polarographic measurements, kindly made by Dr. R. J. Cvetanović, showed that the aldehyde found in the products of EtO isomerization was acetaldehyde.

As described in Parts I and II, the catalyst was conditioned with respect to C_2H_4 oxidation at the working temperatures, and kinetic runs at 274° and 234°C. were made. Subsequently the investigation on EtO was started. It was realized (Part I) that the catalyst conditioned by ethylene oxidation was in a very unsteady state with respect to EtO oxidation. On the other hand, as soon as runs of the latter reaction were made, the catalyst tended to be conditioned by them and behaved, then, inhibited with respect to ethylene oxidation. An explanation of these phenomena is offered in Part I.

As was the case during the study of ethylene oxidation, the obtaining of reproducible results would therefore appear to necessitate catalyst conditioning at the given reaction temperature with a standard gas mixture having average composition respecting the range employed. Runs of short duration were made, followed by the standard mixture. In this way frequent checks of the catalyst's activity and the maintenance of its reference state were achieved.

The symbols for feed composition are similar to those used previously except that instead of E (ethylene) symbol X (ethylene oxide) is used. The arbitrary unit of gas mixture flow rate is 41.8 liters (N.T.P.)/hour. The symbol $[pX_nO_m]$ means 41.8 p liters (N.T.P.)/hour of feed gas mixture having composition 2.35 n% C_2H_4O; 9.90 m% O_2, the remainder being N_2 at a total pressure of 1 atmosphere.

The standard feed for the purpose of conditioning and checking was $1.X_2O_2$.

In the preliminary stages of the work, seven measurements were made to check the material balance of reactants and products (EtO and CO_2). Three of them included C_2H_4 determination. At a later stage analyses for acetaldehyde were made frequently, particularly for the composition X_4O_1, but always with negative result.

Ethylene was determined as described in Part II. The method did not allow detection of less than 0.1–0.2 cc. (N.T.P.) as was shown by blank runs. The results with $1X_2O_2$ and $4X_2O_2$, using gas samples of 250–500 cc. showed that the conversion of EtO to C_2H_4, if any, was below 1%.

The over-all balance was found to be between 97 and 101%* (without counting the possibility of slight C_2H_4 formation).

Therefore all conversions were determined directly by CO_2 analysis instead of indirect determination by EtO analysis.

**There is some indication that during the first 40 min. after admission of $1X_2O_2$ to the catalyst preconditioned by C_2H_4 oxidation, the balance of EtO, CO_2, and possibly C_2H_4 is only about 90%. The data are not sufficient to explain or confirm this behavior.*

TABLE I

OXIDATION OF ETHYLENE OXIDE AT 274°C.

Kinetic run No.	Feed composition symbol	Time operated (hr.)	% EtO to CO_2	Standard check No.
1*a*	$1X_1O_1$	0.65	10.7	—
1*b*	$1X_1O_1$	1.65	10.3	—
1*c*	$1X_1O_1$	2.80	10.2	—
2*a*	$2X_1O_1$	0.65	6.27	—
2*b*	$2X_1O_1$	1.40	6.35	—
—	$1X_2O_2$	0.60	9.00	1*a*
—	$1X_2O_2$	1.20	9.30	1*b**
—	$1X_2O_2$	1.25	8.86	2*a*
—	$1X_2O_2$	3.35	8.65	2*b*
3*a*	$1X_1O_4$	0.65	12.85	—
3*b*	$1X_1O_4$	2.00	12.85	—
—	$1X_2O_2$	0.65	9.46	3*a*
—	$1X_2O_2$	17.00	9.00	3*b*
4*a*	$2X_1O_4$	0.65	8.12	—
4*b*	$2X_1O_4$	2.00	8.30	—
5*a*	$1X_1O_8$	1.00	13.30	—
5*b*	$1X_1O_8$	1.75	13.05	—
6*a*	$2X_1O_8$	0.65	7.22	—
6*b*	$2X_1O_8$	1.35	7.40	—
—	$1X_2O_2$	0.65	9.50	4*a*
—	$1X_2O_2$	17.00	8.95	4*b*
7*a*	$1X_4O_4$	0.65	7.92	—
7*b*	$1X_4O_4$	1.35	8.25	—
7*c*	$1X_4O_4$	2.00	8.39	—
8*a*	$2X_4O_4$	0.65	4.51	—
8*b*	$2X_4O_4$	1.35	4.42	—
9*a*	$4X_4O_4$	0.65	2.84	—
9*b*	$4X_4O_4$	2.00	2.74	—
—	$1X_2O_2$	0.65	8.95	5*a*
—	$1X_2O_2$	18.00	9.46	5*b*
—	$1X_2O_2$	18.75	8.70	5*c*
—	$1X_2O_2$	19.25	8.86	5*d*
—	$1X_2O_2$	20.00	8.66	5*e*
—	$1X_2O_2$	20.75	8.92	5*f*
—	$1X_2O_2$	22.00	8.86	5*g**
—	$1X_2O_2$	1.50	9.70	6*a*
—	$1X_2O_2$	3.65	8.41	6*b*
—	$1X_2O_2$	20.50	8.70	6*c*
11*a*	$2X_2O_2$	0.65	5.30	—
11*b*	$2X_2O_2$	1.35	5.34	—
12	$4X_2O_2$	0.65	3.04	—

**The apparatus was closed down (cooling to room temp. in N_2 stream) after check 1b, 5g, and 10b.*

TABLE I (*Concluded*)

Kinetic run No.	Feed composition symbol	Time operated (hr.)	% EtO to CO_2	Standard check No.
13	$4X_1O_4$	0.65	4.25	—
14	$2X_1O_4$	0.65	7.90	—
15	$1X_1O_4$	0.65	13.45	—
—	$1X_2O_2$	0.65	9.20	7*a*
—	$1X_2O_2$	18.00	9.20	7*b*
16	$4X_1O_8$	0.65	4.20	—
17*a*	$1X_1O_8$	0.65	12.85	—
17*b*	$1X_1O_8$	1.35	12.75	—
—	$1X_2O_2$	0.65	8.82	8*a*
—	$1X_2O_2$	1.50	8.63	8*b*
18*a*	$1X_4O_8$	1.00	8.94	—
18*b*	$1X_4O_8$	1.50	8.65	—
18*c*	$1X_4O_8$	2.75	8.60	—
19*a*	$2X_4O_8$	1.50	5.31	—
19*b*	$2X_4O_8$	2.20	5.52	—
—	$1X_2O_2$	0.65	8.75	9*a*
—	$1X_2O_2$	17.50	9.09	9*b*
20	$4X_4O_8$	0.65	3.09	—
21	$4X_4O_4$	0.65	2.80	—
22	$4X_4O_1$	0.65	1.60	—
23	$2X_4O_1$	1.00	2.62	—
24	$1X_4O_1$	0.65	4.60	—
—	$1X_2O_2$	0.65	11.70	10*a*
—	$1X_2O_2$	1.20	11.30	10*b**
—	$1X_2O_2$	0.65	9.55	11*a*
—	$1X_2O_2$	1.35	9.16	11*b*

**The apparatus was closed down (cooling to room temp. in N_2 stream) after check 1b, 5g, and 10b.*

RESULTS

1. *Oxidation Kinetics at Constant Temperature*

The influence of feed composition and flow rate was studied after overnight stabilization of the catalyst using mixture $1X_2O_2$ in all cases.

Table I shows the results of kinetic runs and of the frequent checks for the standard $1X_2O_2$ feed. Operation times are included in this table.

All checks for $1X_2O_2$ indicated 8.5–9.5% conversion to CO_2 and hence the surface was assumed to be in the same reference state. One exception was the check run $1X_2O_2$ made after studying the composition X_4O_1, where CO_2 conversion of $1X_2O_2$ was found as high as 11.5% during the first few hours.

Hence the values for X_4O_1 are corrected to the normal reference state. This behavior of oxygen deficient feed is very similar to the behavior observed with similar ethylene–oxygen compositions. (Compare feed E_4O_1 in Parts I and II.)

Conversions versus reaction time co-ordinate for different feed compositions are plotted in Fig. 1.

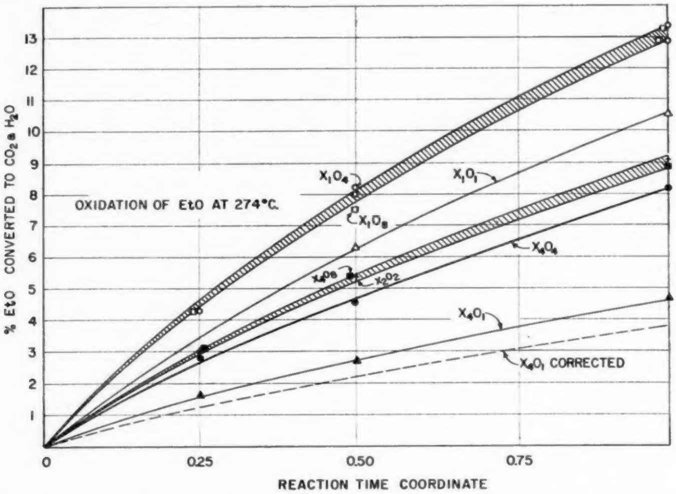

FIG. 1. Conversion of EtO to CO_2 and H_2O at 274°C. vs. reaction time for different feed compositions.

The initial rate of reaction is given by

$$r_0 = V_x \left(dx/d\,\frac{M}{F} \right)_0 \qquad [1]$$

where V_x = volume fraction of EtO in the feed,
x = fraction of EtO converted to CO_2 and H_2O,
M = catalyst quantity (assigned unity and constant throughout),
F = flow rate of feed gas mixture in previously defined arbitrary units,
r = rate of reaction in the same units with $M = 1$.

Suffix $_0$ means conditions at zero reaction time when $M/F = 0$.

The initial rates are shown by the points on Fig. 2.

In Part IV, which deals with reaction mechanism, the reasons will be presented which led to a rate equation of the form

$$r_0 = \frac{A}{1 + \dfrac{B}{p_X} + \dfrac{C}{p_O}} \qquad [2]$$

where p_X = EtO partial pressure
p_O = O_2 partial pressure
A, B, C are constants.

The constants were found by the method of least mean squares to give

$$r_0 = \frac{0.032}{1 + \dfrac{90}{p_X} + \dfrac{270}{p_O}} \quad \text{at } 274°\text{C.}$$

(Partial pressures are expressed in mm. Hg.)

Fig. 2 includes as solid lines the values of rates calculated according to the above equation showing good agreement between experimental and calculated data.

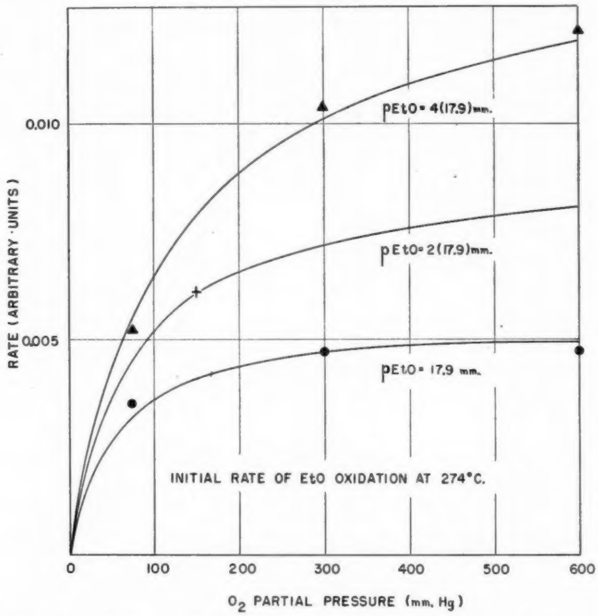

FIG. 2. Initial rate of CO_2–H_2O formation from EtO at 274°C. as a function of reactant partial pressures.

It is noteworthy that the equation obtained is very similar to the one derived for C_2H_4 oxidation (Part II), except for the constant A.

2. *Oxidation Temperature Dependence*

A few measurements were made shortly after the temperature was changed, and are presented in Table II. (Times necessary for heating or cooling to the required temperature were usually in the order of half an hour.) These are not the steady values which would have been obtained after very prolonged opera-

TABLE II
TEMPERATURE DEPENDENCE
OXIDATION OF ETHYLENE OXIDE (FEED $1X_2O_2$)

T, °C.	Time operated at T°C. (hr.)	Sample No.	% EtO to CO_2
274	17.70	4	8.55
254	0.25	1	5.6
254	0.75	2	4.9
254	1.50	3	4.9
294	0.16	1	14.3
294	0.66	2	12.5
274	0.16	1	8.5
274	0.83	2	8.4
274	1.83	3	8.7
274	19.50	4	8.9

tion where slow processes have changed the nature of the catalyst (compare Part I). Therefore they indicate more correctly the dependence of kinetics on temperature. Checks at 274°C. after operating at other temperatures included in Table II prove indeed that the reference state of the surface has been maintained throughout.

3. *Isomerization to Acetaldehyde*

Immediately following the kinetic runs for EtO oxidation, the investigation of EtO isomerization at 274°C. was begun by feeding only EtO and N_2. All data are presented in Table III.

In Expt. 3, after 2.25 hr. operation, a check was made for the presence of C_2H_4 in the outgas. This, if any, corresponded to less than 0.6% conversion of EtO. The over-all balance of EtO was also within the limits of experimental error.

In view of the absence of C_2H_4, the formation of CO_2 seems surprising. If the oxygen were supplied by decomposition of EtO, according to:

$$5\ C_2H_4O \rightarrow 5\ C_2H_4 + 2.5\ O_2$$
$$C_2H_4O + 2.5\ O_2 \rightarrow 2\ CO_2 + 2\ H_2O$$

then for each mole of EtO converted to CO_2, there would be 5 moles of EtO converted to C_2H_4. The conversion to CO_2 being of the order of 2%, this would result in conversion to C_2H_4 of the order of 10%, which is not the case. Also, the adsorption capacity of the catalyst is far too small to account for the missing C_2H_4.

It is therefore concluded that the N_2 employed contained small amounts of oxygen which are responsible for CO_2 formation; 0.2–0.5% of O_2 in nitrogen might be sufficient quantitatively, based on the kinetics of EtO oxidation. The conversion to CO_2 increases with decreasing EtO pressure (compare Expts. 6 and 8 in Table III) which also conforms to the kinetics of EtO oxidation but is not paralleled by the behavior of isomerization in the same experiments.

TABLE III

ISOMERIZATION OF ETHYLENE OXIDE TO ACETALDEHYDE

Flow composition symbol	Time operated (hr.)	% EtO converted			Expt. No.
		To CH_3CHO	To CO_2	Total	
$1X_2O_0$	0.40	2	—	—	1
$1X_2O_0$	0.85	2	—	—	1
$1X_2O_0$	1.50	2	—	—	1
$1X_2O_2$	0.33	—	9.78	—	2 Oxidation
$1X_2O_2$	0.85	—	9.10	—	2
$1X_2O_2$	17.50	—	9.16	—	2
$1X_2O_0$	0.16	2.1	—	—	3
$1X_2O_0$	0.55	1.6	—	—	3
$1X_2O_0$	1.50	1.5	—		3
$1X_2O_0$	2.25	—	1.7	3.2	3
$1X_2O_0$	4.00	—	1.6		3
$1X_2O_0$	4.67	1.25	—	2.9	3
$1X_1O_0$	0.33	0.85	—	—	4
$1X_1O_0$	0.66	0.85	—	—	4
$1X_1O_0$	0.90	0.85	—	—	4
$1X_2O_0$	0.33	1.35	—	—	5
$1X_2O_0$	18.00	0.67	—	—	5
$1X_4O_0$	0.40	—	1.3		6
$1X_4O_0$	0.75	0.87	—	2.2	6
$1X_4O_0$	1.00	0.87	—		6
$1X_4O_0$	1.25	—	1.2	2.1	6
$0.25X_4O_0$	0.40	—	1.85		7
$0.25X_4O_0$	0.90	3.0	—	4.9	7
$0.25X_4O_0$	1.25	—	2.0	5.0	7
$1X_1O_0$	0.40	—	3.6		8
$1X_1O_0$	0.75	0.28	3.6	3.9	8
$1X_2O_0$	0.50	0.56	—	—	9
$1X_2O_2$	0.16	—	13.4	—	10 Oxidation
$1X_2O_2$	0.33	—	11.4	—	10
$1X_2O_2$	0.90	—	10.1	—	10
$1X_2O_2$	17.65	—	8.55	—	10
After 58 hr. $(1E_2O_2)$					
X_2O_0	0.25	2.4	—		11
X_2O_0	0.58	—	1.2	3.6	11
X_2O_0	0.83	1.95	—	3.2	11
X_2O_0	1.25	—	1.2	3.1	11
X_2O_0	1.80	1.50	—	2.7	11
X_2O_0	2.75	—	1.2	2.7	11
X_2O_0	3.00	1.30	—	2.5	11
X_2O_0	18.00	0.80	—		11
X_2O_0	18.25	—	1.2	2.0	11

DISCUSSION

1. Oxidation

Twigg (1) reported that EtO is oxidized on silver catalyst, but there is little information concerning the kinetics of this reaction. Also there are

insufficient data relating to rate of C_2H_4 formation, especially at small reaction times.

There were, a priori, three possibilities:

1. EtO is oxidized without previous dissociation into C_2H_4 and O_2.
2. EtO is decomposed into C_2H_4 and O_2* followed by oxidation of C_2H_4, with no EtO being oxidized directly.
3. EtO undergoes simultaneous direct oxidation and dissociation to O_2 and C_2H_4, the latter being subject to further oxidation.

The present data substantiate statement (1) for the main reaction step, since C_2H_4 did not occur in detectable quantities in the products.

The dependence of oxidation rate on the reactant partial pressures excludes isomerization of EtO on the Ag surface as a main step in its oxidation, because there is no reason for isomerization to increase with oxygen pressure. Instead, it is suggested that one of the following mechanisms is responsible for the formation of intermediates, which are then capable of undergoing rapid oxidation.

(*a*) Reaction between EtO and an oxygen adatom, adsorbed side by side.

(*b*) Collision of a gaseous EtO molecule with an oxygen adatom.

In accordance with this (see discussion below) the rate of EtO isomerization to acetaldehyde is shown to be substantially lower than the rate of EtO oxidation.

A private communication from industrial sources claimed that the rate of EtO oxidation passes through maximum at 260°C. This would imply that mechanism (*a*) may be valid where EtO desorption rates become comparable with oxidation rates at approximately 260°C.

We were unable to observe such an effect (Table II) and therefore believe that the mechanism (*b*) cannot be excluded.

The present data may be compared with those for C_2H_4 oxidation (Part II). It transpires that the same factors favorable to high conversions of ethylene to EtO in the initial stages of the reaction are also operative for the conversion of EtO to CO_2. Those factors are: large oxygen partial pressure and low oxygen acceptor pressure. Therefore a high $p_{O_2}/p_{C_2H_4}$ ratio does not necessarily represent the best operating conditions for EtO production as was pointed out previously (Part II).

The present data may be helpful in attempting to correlate the reaction rate data for the over-all C_2H_4 oxidation as a function of contact time.

Before this can be done, however, more data are needed for the influence of CO_2 and H_2O. Also the effect of the initial composition ratio $p_{C_2H_4}/p_{C_2H_4O}$ should be investigated, which could be followed experimentally by using carbon-labelled EtO. This method would provide further evidence for the formulation of a reaction mechanism.

2. Isomerization

The quantitative interpretation of the isomerization process is unfortunately obscured by the presence of oxygen traces in the diluent N_2 and influenced

**This was actually found to occur by Twigg (1) when EtO is admitted to oxygen free silver in a static system.*

adversely by the difficulty of estimating low concentrations of acetaldehyde in the products. Furthermore, the conversion level is not steady. Higher conversions to acetaldehyde (about 2%) are obtained immediately after pretreatment by EtO oxidation (Expts. 1 and 3, Table III) or by C_2H_4 oxidation (Expt. 11). Further, the isomerization decreases with operating time. This confuses the interpretation of data but might indicate the formation of a surface deposit. It will be noted that the standard oxidation of ethylene oxide (Expt. 10) gives higher than normal values: 13.4% instead of 9%, when made immediately after the series of isomerization runs. The same is true if C_2H_4 oxidation is run after isomerization: initially, abnormally high conversions both to CO_2 and to EtO are obtained as described in Part I. The adsorption capacity of the catalyst used (about 1 cc. N.T.P.) seems too small to explain this excess conversion only on the basis of a deposit which burns on contact with O_2.

This behavior could be explained if we assume that feeding EtO with practically no oxygen is effective as follows:

(*a*) stably sorbed oxygen, inhibiting the reaction (see Part I) is removed;

(*b*) the surface is slowly covered by acetaldehyde residues.

When oxygen is admitted later, together with C_2H_4 or EtO, the acetaldehyde residues are burned off immediately. The fixation of oxygen in stable positions and the formation of oxidation residues (see Part I) being slow, the rate of oxidation during the first few hours will be greater than normal on this cleaned surface.

Notwithstanding the complications due to the unsteady level of isomerization and to the presence of oxygen, it appears that isomerization increases with increasing EtO pressure (comparing Expts. 3, 4, and 5; 6 and 8; 8 and 9). This is expected since the rate of isomerization will be proportional to the fraction of Ag surface covered by adsorbed EtO, and this must increase with its pressure.

As was pointed out in the discussion of EtO oxidation, the kinetics of this reaction do not conform to the hypothesis that isomerization to acetaldehyde is the rate determining stage during oxidation. To support the independent direct oxidation of EtO as the main path of CO_2 formation it should be possible to show that isomerization of EtO to acetaldehyde is slower than the oxidation of EtO under comparable conditions.

Experiments 2 and 3 in Table III show that initial conversion to acetaldehyde is 2.1% against about 9% conversion to CO_2, when oxygen is present. Thus, less than 25% of EtO oxidized undergoes isomerization. Moreover the conditions of Expts. 2 and 3 are not strictly comparable because in the latter case, the available free Ag surface is increased in the absence of oxygen, and consequently measured values for isomerization could be actually higher than those which occur during oxidation.

The CO_2 conversions shown in Table III can be attributed without difficulty to the direct oxidation of EtO by traces of oxygen. On the other hand, if it is assumed that all CO_2 shown in Table III arises by prior isomerization followed by oxidation due to traces of oxygen, the highest isomerization values would be

3.6% (Expt. 11). This would still account for only 40% of the EtO which is oxidized under comparable conditions.

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THE SILVER CATALYZED OXIDATION OF ETHYLENE

IV. REACTION MECHANISM[1]

By A. Orzechowski and K. E. MacCormack[2]

ABSTRACT

A reaction mechanism for the silver catalyzed oxidation of C_2H_4 by oxygen has been formulated which is consistent with kinetic data for this system. It is suggested that both ethylene oxide and CO_2 formation involve interaction of single gaseous C_2H_4 molecules with single oxygen adatoms. This may be a system of two parallel reactions of different activation energy requirements or a common initiation step to form adsorbed ethylene oxide which may then desorb immediately or isomerize to acetaldehyde followed by rapid oxidation to CO_2 and H_2O. Account is taken of the known adsorption characteristics of O_2 on silver to deduce expressions for initial rates of ethylene oxide and CO_2 formation as a function of reactant partial pressures. The generalized form of the equation is $r = k(1 + a/p_E + b/p_O)^{-1}$, where k, a, and b are temperature dependent constants and p_E and p_O are partial pressures of ethylene and of oxygen respectively.

A mechanism is also suggested for the heterogeneous oxidation of ethylene oxide which involves interaction between a gas phase ethylene oxide molecule and a single oxygen adatom to form an intermediate (probably formaldehyde) which is rapidly oxidized to CO_2 and H_2O. A similar expression to that above for the initial oxidation rate is deduced. These expressions have been fitted successfully to experimental data.

The experimental data presented in the previous parts (I–III) of this series of publications have been used to formulate a consistent reaction mechanism for ethylene oxidation on silver. It was shown in Part II that only two parallel reactions can account for the production of ethylene oxide (EtO) on the one hand (rate, r_1), and CO_2 and H_2O on the other (rate, r_2) from C_2H_4 and oxygen. Initially these exist alone but are accompanied during the course of the reaction by a slow consecutive oxidation of EtO. Though the major part of CO_2 formation arises from C_2H_4, this does not exclude the possibility that adsorbed EtO (as opposed to desorbed EtO) formed by C_2H_4 adsorption on an oxygen adatom, is the intermediate in the so-called direct oxidation of C_2H_4 to CO_2 and H_2O. This point will be expanded later.

Further, the initial selectivity given by the expression $r_1/(r_1 + r_2)$ appears to be dependent only on temperature and not on reactant composition provided the same catalyst reference state is carefully maintained as described in the earlier parts of this series. Consequently, the two primary reactions show the same initial rate dependence on reactant concentrations and may well proceed through the same type of, if not a common reaction step. This is in contrast to the opinion expressed by Twigg (5) who proposed two dissimilar steps,

$$C_2H_4 \text{ (gas)} + \ 0 \text{ (ads.)} \rightarrow C_2H_4O,$$

$$C_2H_4 \text{ (gas)} + 20 \text{ (ads.)} \rightarrow CO_2 + H_2O \text{ (via short-lived intermediates)}.$$

In considering data for the initial stages of the reactions the influence of products may be neglected. The known adsorption characteristics of the

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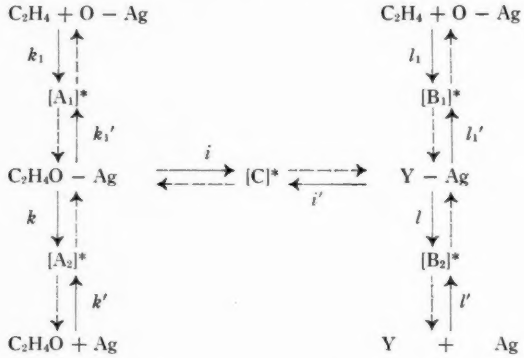
[2] *National Research Council Postdoctorate Fellow, 1951–53.*

reactants suggest that the initial reaction step involves impact of gaseous C_2H_4 with adsorbed oxygen. It is proposed that only single adatoms of the latter are involved, according to the reaction scheme presented below.



A*, B*, and C* are activated complexes with k, l, and i, the velocity constants of the various rate determining steps. Y is isomeric with EtO and is very rapidly oxidized to CO_2 and H_2O. In several respects, this scheme is similar to that proposed by Twigg. The direct oxidation to EtO follows the path k_1k with his observed reverse reaction $k'k_1'$. In agreement with the present work (Part III) EtO was found to isomerize to $CH_3.CHO$ in the absence of O_2 which is represented by the path $k'il$ and Y would thus be identified as $CH_3.CHO$.

It follows then that one possible path for the direct production of CO_2 from C_2H_4 is through adsorbed EtO (k_1il) in contrast with any postulation concerning separate deep oxidation of C_2H_4 by its reaction with either single or paired O_2 adatoms. However, since the present evidence does not allow differentiation between identical and similar primary steps for the formation of both EtO and CO_2, it is also necessary to introduce the other possible step (l_1l) by which the same isomer Y can be formed with different activation energy requirements. In both cases, however, only single oxygen adatoms are proposed.

Although some acetaldehyde is formed via $k'il$ when EtO is placed in contact with Ag, it was shown in Part III that this reaction cannot be considered the rate determining step in the oxidation of EtO. Another independent reaction was proposed which involved either (*a*) surface reaction between adsorbed EtO and an oxygen adatom, or (*b*) reaction between gaseous EtO and an oxygen adatom. If the latter mechanism be correct, its influence on the kinetics of C_2H_4 oxidation need not be considered under conditions where the gas phase concentration of EtO may be neglected. If, however, mechanism (*a*) were valid, its bearing on the interpretation of the kinetics of C_2H_4 oxidation becomes important depending on the fraction of surface (ϵ) covered by adsorbed EtO, (1) during C_2H_4 oxidation (ϵ_1) and (2) during EtO oxidation (ϵ_2).

This may now be considered in relation to the path by which the major part of CO_2 is produced during C_2H_4 oxidation. It will be recalled that under com-

parable conditions the conversion of C_2H_4 to CO_2 is greater* than the conversion of EtO to CO_2. Allowing $\epsilon_1 \ll \epsilon_2$ which would occur for $k_1 \ll k'$, the C_2H_4 oxidation mechanism by isomerization of adsorbed EtO (path i) would not account for the greater CO_2 production. Therefore the independent path l_1 has to be introduced to account for the major CO_2 producing reaction. This would be equally necessary if mechanism (a) above were valid in the oxidation of EtO.

Assuming the alternative case of $\epsilon_1 \gg \epsilon_2$ where $k_1 \gg k'$, deep oxidation of C_2H_4 to CO_2 via the isomerization path i could account for the major part of the CO_2 produced and step l_1 would be unnecessary. In this case EtO oxidation by mechanism (a) must be excluded for otherwise the initial selectivity during C_2H_4 oxidation would show a dependence on reactant concentration.

The above may be summarized as follows:

$\epsilon_1 \ll \epsilon_2$; oxidation of C_2H_4, step l_1 necessary; oxidation of EtO, mechanism (a) or (b) valid.

$\epsilon_1 \gg \epsilon_2$; oxidation of C_2H_4, step l_1 unnecessary; oxidation of EtO, mechanism (a) excluded.

Oxygen Adsorption

One of the chief difficulties in the mathematical interpretation of the mechanism of C_2H_4 oxidation lies in assessing the part played by oxygen adsorption.

At temperatures within the range studied during the present work it is known (1) that the adsorption is extremely rapid, decreasing very quickly with extent of surface coverage. Desorption is extremely slow and may thus be neglected in estimating the surface coverage during the oxidation of C_2H_4. Since C_2H_4 adsorption on Ag can be neglected (5), oxygen adsorption is obviously prerequisite to reactions with C_2H_4.

Information concerning the adsorption of O_2 on a similar silver catalyst has been communicated privately by Drs. E. L. Tollefson and W. Smeltzer. Rates were measured between 200 and 300°C. at constant pressures ranging from 200 to 700 mm. Hg. In every case the surface attains at least 50% of its equilibrium coverage corresponding to given values of pressure and temperature in less than 0.1 min. and over this region the rate of adsorption appears to be directly proportional to the pressure. The maximum amount of O_2 sorbed by a 50 gm. sample was 5.4 cc. (N.T.P.) at 200°C. and 700 mm. Hg. After deduction of 0.7 cc. which according to the data of Steacie and Johnson (3) could dissolve in Ag under these conditions, there remains a minimum value of 4.7 cc. for O_2 adsorption when θ, the fractional surface coverage, becomes

**In Part I, dealing with slow processes, it was shown that quantitative replacement of C_2H_4 undergoing oxidation (35% conversion to CO_2) by EtO involved an initial decline to about 5–10% conversion to CO_2, then passage through a maximum of 17% and finally a stable level of 9% (Fig. 5). The immediate return to C_2H_4 oxidation showed an initial conversion to CO_2 of only 10% (Fig. 3) slowly increasing to the previous level of 35%. Thus a change from C_2H_4 to EtO oxidation indicates higher rates of CO_2 production for the former, whereas a change in the opposite direction shows similar rates at least initially. In no case is the rate of CO_2 formation greater for EtO than for C_2H_4 oxidation. The possible explanation of these effects is that EtO admitted after C_2H_4 undergoes oxidation mainly via the isomerization step. The slow development of surface residues causes a decline in the part played by this mechanism relative to that of the direct oxidation step described. Consequently, the return to C_2H_4 oxidation on the poisoned surface shows a correspondingly low conversion to CO_2, slowly increasing with the removal of surface residues.*

unity. In all cases, during the first 0.1 min., the derived values of θ are less than 0.65. At 0.2 min. the rate falls to less than 0.03 of the average rate during the first 0.1 min., followed by further rapid decline. It is reasonable to infer that initial rates at very low coverage will be very fast.

Comparing the above adsorption sample with the catalyst sample used in the present work (12 gm.) and assuming the same surface properties, calculation shows that the O_2 adsorption rate during the catalyzed C_2H_4 oxidation is rather greater than the average rate estimated from the Tollefson–Smeltzer data up to $\theta = 0.65$. For example, by interpolation and extrapolation of the latter results at 75 mm. Hg and 234°C. the average O_2 adsorption rate during the first 0.1 min. is 3.5 cc./min. (for 12 gm.). The O_2 adsorption rate deduced from C_2H_4 oxidation data at the same temperature and O_2 pressure and with C_2H_4 partial pressure = 72 mm. Hg, is 7 to 25 cc./min. (for 12 gm.) depending on the selectivity and mechanism of the direct oxidation to CO_2. Therefore, during the catalyzed oxidation of C_2H_4 it can be inferred that the Ag surface is quite sparsely covered by O_2.

Although the dependence of adsorption rate on coverage below $\theta = 0.3$ is too fast to be measured accurately at temperatures in the order of 250°C., the data of Tollefson and Smeltzer as well as an extrapolation of Benton and Drake's data (1) indicate the possibility of large decrease of adsorption rate with increasing θ even for $\theta < 0.3$.

Taylor and Thon (4) have recently shown that in many cases adsorption rates obey the equation $dq/dt = ae^{-bq}$, where q is the amount adsorbed in time, t, with b constant and a, a function of the pressure. This is substantiated by recent measurements of Porter and Tompkins (2). In addition it is also possible to fit the data of Benton and Drake (1) to an equation of this type, one valid for the approximate range $0.3 < \theta < 0.5$, another for the range $0.5 < \theta < 0.7$. In each range a is directly proportional to the oxygen pressure.

A series expansion of the Taylor–Thon equation, using θ in place of q and retaining only the first two terms gives

$$d\theta/dt = jp_{\mathrm{O}}(1 - m\theta) \tag{1}$$

where $a = jp_{\mathrm{O}}$ (j = const.) and $b = m$.

SURFACE COVERAGE BY REACTING SPECIES

Considering C_2H_4 oxidation under initial conditions of reaction, let

p_{O}, p_{E} = the partial pressures of O_2 and C_2H_4 respectively,

θ = fraction of catalyst surface covered by O_2 atoms,

α = fraction of this O_2 layer covered by C_2H_4 adsorbed in any form,

β = fraction of C_2H_4 adsorbed on the O_2 layer which can be identified as EtO adsorbed on Ag.

The velocity constants are used according to the foregoing reaction scheme.

I. Steady State Balance of EtO in the Adsorbed Phase

At the steady state the formation rate of adsorbed EtO by reaction between C_2H_4 and O_2 adatoms and by reverse isomerization of Y will be balanced by its removal by desorption, by decomposition into C_2H_4 and O_2 adatoms, and by

isomerization to Y. This may be expressed

$$k_1 p_E(1-\alpha)\theta + i'\alpha\theta(1-\beta) = k\alpha\theta\beta + k_1'\alpha\theta\beta + i\alpha\theta\beta$$

or,

$$k_1 p_E(1-\alpha) = \alpha[\beta(k + k_1' + i + i') - i']. \tag{2}$$

II. Steady State Balance of Y in the Adsorbed Phase

By argument similar to that above,

$$l_1 p_E(1-\alpha)\theta + i\alpha\theta\beta = l\alpha\theta(1-\beta) + l_1'\alpha\theta(1-\beta) + i'\alpha\theta(1-\beta)$$

or,

$$l_1 p_E(1-\alpha) = \alpha[(1-\beta)(l + l_1' + i + i') - i]. \tag{3}$$

Dividing equation [1] by equation [2]

$$\beta = \text{a function only of the velocity constants,}$$
$$= \text{constant at constant temperature.}$$

Therefore each of the expressions contained by square brackets in equations [2] and [3] is constant.

$$\therefore \alpha/(1-\alpha) = Ap_E \quad \text{or} \quad \alpha = Ap_E/(1 + Ap_E) \tag{4}$$

where A is a constant at constant temperature.

III. Steady State Balance of O_2 Atoms in the Adsorbed Phase

At the steady state, the rate of formation of oxygen adatoms both by O_2 adsorption and by decomposition of adsorbed isomers of EtO with reconstitution of ethylene will be balanced by removal of O_2 adatoms as a result of C_2H_4 adsorption on these atoms and the possible heterogeneous oxidation of gaseous Y. Consecutive oxidation of Y is known to be very much more rapid than that of gaseous EtO as no Y can be detected in the gas phase.

Neglecting the rate of desorption of O_2 and writing the adsorption rate according to equation [1], we have,

$$jp_O(1 - m\theta) + [k_1'\beta + l_1'(1-\beta)]\alpha\theta = (k_1 + l_1)p_E(1-\alpha)\theta + nl\alpha\theta(1-\beta) \tag{5}$$

where n is the number of O_2 adatoms used in the heterogeneous oxidation of one molecule of Y. With $0 < n < 5$, equation [5] gives,

$$\theta = \frac{jp_O}{jp_O m + (k_1 + l_1)(1-\alpha)\,p_E + [nl(1-\beta) - k_1'\beta - l_1'(1-\beta)]\alpha}. \tag{6}$$

Now, the rate of formation of EtO (r_1) is given by,

$$r_1 = k\alpha\theta\beta \tag{7}$$

and the rate of formation of CO_2, (r_2) is given by,

$$r_2 = l\alpha\theta(1-\beta). \tag{8}$$

Combining equations [4], [6], and [7], we have,

$$r_1 = \frac{k\beta/m}{1 + (1/Ap_E) + (B/jmp_O)} \tag{9}$$

where $B = (k_1 + l_1)/A + nl(1-\beta) - [k_1'\beta + l_1'(1-\beta)]$
$= \text{constant at constant temperature.}$

Inspection of equations [7] and [8] indicates that r_2 may be represented by an expression similar to equation [9] except that the numerator will be $l(1-\beta)/m$ instead of $k\beta/m$.

As was demonstrated in Part II of this series, the dependence of initial reaction rates on reactant partial pressures obeyed the relationship derived in equation [9], which lends support to the over-all reaction mechanism proposed.

It is now possible to discuss further the consistency of equation [1] with respect to the experimental data and the adsorption concepts offered. Equation [6] may be written in the form,

$$m\theta = \frac{1}{1 + \alpha B/jmp_{\mathrm{O}}} \tag{10}$$

from which values of $m\theta$ may be computed knowing α by equation [4], the over-all constants A and B/jm being given by fitting equation [9] to the experimental rate data. The following table shows the calculated range of values of $m\theta$.

Temp., °C.	p_{O}, mm. Hg	p_{E}, mm. Hg	$m\theta$
234	600	18	0.88 max.
	75	72	0.34 min.
274	300	18	0.88 max.
	75	72	0.43 min.

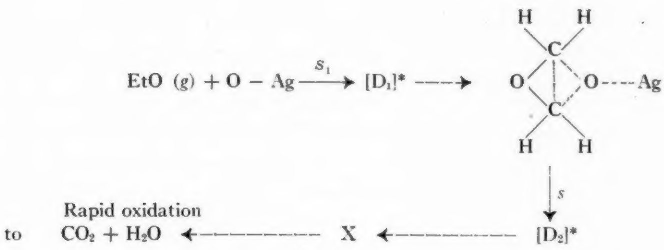
The range of variation of $m\theta = 0.34$ to 0.88 so that m should be at least in the order of 3. In this case θ would vary from about 0.1 to 0.3. Lower values of m would broaden the range of θ too greatly to permit use of the approximate equation [1]. These values of θ are also consistent with values inferred and discussed earlier respecting the extent of O_2 adsorption.

The proposed mechanism may apply equally well to homogeneous and heterogeneous catalyst surface. In the latter case one of the several crystal planes could be preponderantly active for one type of reaction (e.g., k_1k or l_1l). Selective poisoning, referred to in Part I, may be attributed to preferential poisoning of one or other of these planes or to the establishment of impurity centers with consequent influence on the activation energies of the several reaction paths. The latter would be the only possible explanation of these effects in the case of a homogeneous surface.

APPENDIX

Suggested Mechanism for the Heterogeneous Oxidation of EtO

With reference to the previously written reaction scheme, it is assumed that $k' \ll k$ implying that the fraction of catalyst surface covered by adsorbed EtO may be neglected during EtO oxidation. It is suggested that the reaction occurs by impact of gaseous EtO with an adsorbed oxygen atom, according to the following scheme.



Heavy arrows indicate the relatively slow rate determining steps with rate constant s_1 and s for the formation of intermediate activated complexes $[D_1]^*$ and $[D_2]^*$ respectively. The resulting intermediate X (which could be formaldehyde) is rapidly oxidized by either heterogeneous or homogeneous steps.

Let θ = fraction of catalyst surface covered by adsorbed oxygen,
ϕ = fraction of θ covered by EtO adsorbed on oxygen,
p_O, p_X = the partial pressures of O_2 and EtO respectively.

1. Steady State Balance of EtO Adsorbed on Oxygen

The rate of adsorption of EtO on the oxygen layer is balanced by the rate of its reaction. The rate of evaporation is omitted for simplicity as its inclusion will not change the form at any of the subsequent mathematical expressions.

$$s_1 p_X \theta(1 - \phi) = s\theta\phi$$

Hence,

$$\phi = s_1 p_X/(s + s_1 p_X). \qquad [11]$$

2. Steady State Balance of O_2 in the Adsorbed Phase

The rate of adsorption of oxygen adatoms is balanced by their rate of removal due to EtO adsorption on the oxygen layer and to heterogeneous oxidation of X. If n is the number of oxygen adatoms required for the oxidation of X, the following relation exists,

$$jp_O(1 - m\theta) = s_1 p_X \theta(1 - \phi) + ns\theta\phi. \qquad [12]$$

The rate of removal by reaction of EtO is given by,

$$R = s\theta\phi$$

which in conjunction with equations [11] and [12] becomes

$$R = \frac{s/m}{1 + s/s_1 p_X + s(n + 1)/jmp_O}. \qquad [13]$$

This type of equation has been found to account satisfactorily for experimental values of the initial rate of EtO oxidation (see Part III), which is support for the proposed mechanism. Nevertheless, as was indicated earlier, the mechanism involving surface reaction between adsorbed EtO and oxygen adatoms cannot be regarded as impossible. However, mathematical treatment of this system becomes exceedingly complex.

It is interesting to compare the values of θ for C_2H_4 and EtO oxidation. Values of $m\theta$ can be calculated as for C_2H_4 oxidation, using equations [11], [12], and [13]. Equations [9] and [13] can be seen to have the same form. The overall constants (see equation [2], Part II, and equation [2], Part III) of the denominators were found to have very similar numerical values at 274°C. This means that for

[14] $$p_E = p_X, \text{ and } (p_O)_1 = (p_O)_2,$$
$$(m\theta)_1 = (m\theta)_2$$

where subscripts $_1$ and $_2$ refer to C_2H_4 and EtO oxidation respectively.

Hence either

[15] $$m_1 = m_2 \text{ and } \theta_1 = \theta_2$$

or,

[16] $$m_1/m_2 = \theta_2/\theta_1 \text{ with } m_1 \neq m_2.$$

In developing an equation for the rate of O_2 adsorption it will be recalled that a large decrease of the rate with increasing θ was assumed, and m = constant was an approximation valid to account for the rate dependence on θ only over narrow ranges of θ. If θ_1 is very different from θ_2 equation [16] will apply.

The rate of reaction and therefore the rate of oxygen adsorption was found to be several times greater for C_2H_4 than for EtO oxidation. Hence, for $p_E = p_X$ and for $(p_O)_1 = (p_O)_2$ we have,

[17] $$[jp_O(1 - m\theta)]_1 > [jp_O(1 - m\theta)]_2.$$

From equations [14] and [17] we get,

$$(j)_1 > (j)_2.$$

This result can be explained on the basis of different states of catalyst activity during kinetic runs for each of the reactions. It was found that following EtO oxidation runs, the catalyst was appreciably poisoned for C_2H_4 oxidation (see Part I).

Calculation of Integral Conversions

A final test of any rate equation which may be developed theoretically is its successful comparison with experimental conversion data by substitution and integration of the differential reaction rate equations (e.g. Equation 1, Parts II and III).

Thus

$$\frac{M}{F_E} = \int_0^x \frac{dx}{r}.$$

Knowing the activities of the various components of the system as a function of M/F_E, the constants of the r function may then be tested by integration. The values of x thus obtained should be comparable with experimental values.

The theoretical development of the rate equations for both EtO production and its heterogeneous oxidation are based on zero time or initial reaction conditions where the inhibiting effects of reaction products may be neglected.

This has been stressed in the Discussion of Parts II and III. For this reason it is not justifiable to apply these equations in the type of calculation described above. Numerical tests show that graphically measured differential reaction rates for EtO production at various values of the reaction time co-ordinate are very much lower than those calculated on the basis of the initial rate equation; the similarly calculated rate of EtO oxidation is too small to account for this difference. The maxima in conversion/time curves for EtO, occur when the rate of production of EtO is balanced by its oxidation rate. It must be assumed then that there is a functional dependence of EtO production rate on product concentration whose exact nature remains to be determined by further experimental work where products are included in the feed gas.

ACKNOWLEDGMENTS

The authors are particularly indebted to Drs. I. E. Puddington, S. Chu Liang, and J. S. Dugdale for their continued interest and suggestions during the course of this work and to the late Dr. A. Cambron under whose direction and advice it was begun. It is also desired to express appreciation of the assistance of Messrs. F. Liuzzo and J. K. Waterman in the construction and maintenance of the apparatus.

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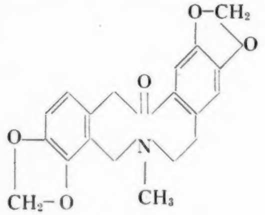
NOTE

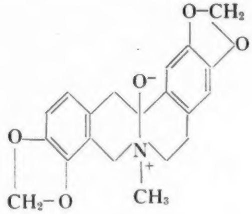
THE STRUCTURE OF PROTOPINE METHIODIDE: A CORRECTION[1]

By F. A. L. Anet[2] and Léo Marion

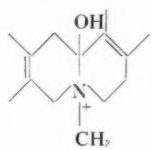
The recent work of Anet, Bailey, and Robinson (1) and of Mottus, Schwarz, and Marion (3) has shown that interaction between a tertiary nitrogen atom and a suitably placed carbonyl group in a large ring can take place. One of the examples chosen by the latter authors was protopine (I) which was shown to give salts with mineral acids by the addition of a proton to the carbonyl oxygen as in (II). In agreement with this it was mentioned that the metho-salts contained no carbonyl band in their infrared spectra and had the new methyl group on the oxygen atom as in (III) (at least in the solid state). The base itself was considered as a resonance hybrid between (I*a* and I*b*).



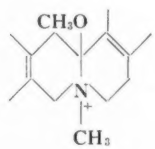
Ia



Ib

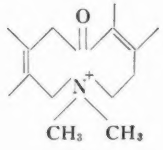


II



III

The former authors (1) working with cryptopine (the dimethoxy analogue of protopine) obtained similar results as far as the structures of the base and ordinary salts were concerned, but found that cryptopine methiodide had an infrared spectrum containing a carbonyl absorption band and so must have structure IV.



IV

[1] *Issued as N.R.C. No. 3222.*
[2] *National Research Council of Canada Postdoctorate Fellow.*

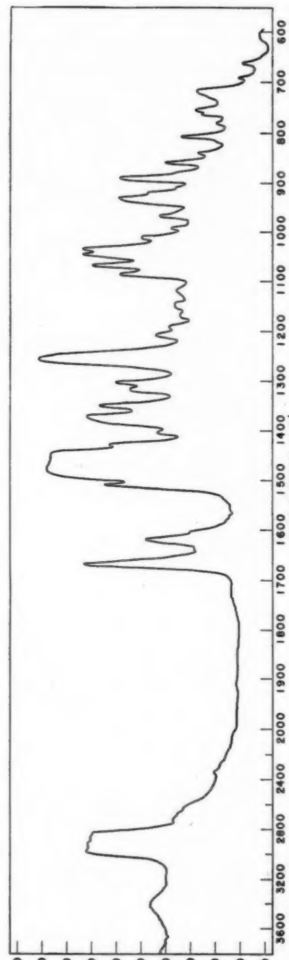


FIG. 1. Infrared spectrum in a nujol mull of protopine methiodide taken on a Perkin-Elmer double beam spectrophotometer model 21.

In view of the close relationship of the two alkaloids this difference in structure of the metho-salts was contrary to what might have been expected. A reinvestigation of the problem has shown that the "protopine methiodide" of Mottus, Schwarz, and Marion (3) was actually protopine hydriodide whose infrared spectrum (which contains a strong bonded hydroxyl band) was identical with that published for the supposed protopine methiodide. Authentic protopine methiodide has now been examined and its infrared spectrum did indeed show a carbonyl absorption band (Fig. 1). It, like cryptopine methiodide but unlike the two parent alkaloids, also gave an immediate color with *m*-dinitrobenzene and alkali in the cold showing the presence of a reactive methylene group.

The above findings remove the necessity for postulating equilibria of various forms of protopine methiodide in solution. The structure of protopine methiodide is then (IV), which is the only form consistent with the chemical evidence of Perkin (4). It might be stated that the negative result in the Zeisel determination of protopine methiodide (3) is not in itself evidence against the methoxy structure, as the proximity of the quaternary nitrogen atom would hinder the addition of a proton to the oxygen atom of the methoxyl group, thus making hydrolysis more difficult than usual. This situation indeed occurs in the metho-salts of *N*-methyl *sec.pseudo*-strychnine (and almost certainly of those of vomicine), which were found by Anet, Bailey, and Robinson (1) to have a methoxy structure, but which are reported by Leuchs (2) to give no methyl iodide in the Zeisel determination.

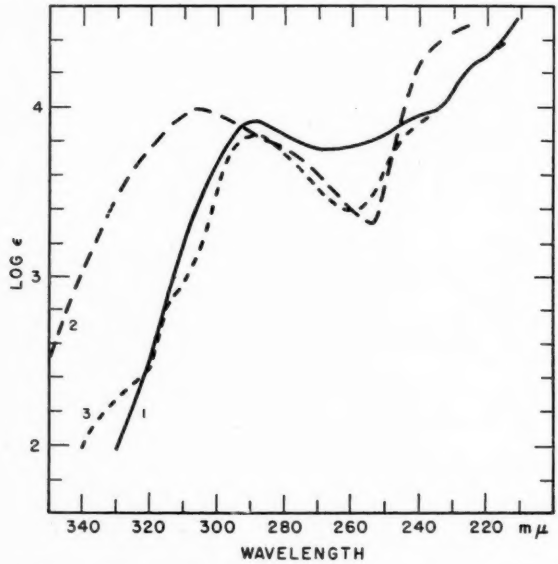


FIG. 2. Ultraviolet spectra in alcohol, curve 1, protopine; curve 2, protopine methiodide; curve 3, protopine hydriodide.

Models of protopine methiodide indicate that the carbonyl group can conjugate to some extent with the adjacent benzene ring, and this is confirmed by the ultraviolet spectrum (Fig. 2) as well as by the position of the carbonyl band in the infrared spectrum. This band (1667 cm.$^{-1}$) is at appreciably lower wave numbers than that of acetophenone (1690 cm.$^{-1}$) but it is close to the more comparable acetoveratrone (1670 cm.$^{-1}$). The photographs of models of protopine given by Mottus *et al.* (3) show that the carbonyl group is very much out of the plane of the benzene ring when in position for favorable interaction with the nitrogen atom. As the carbonyl band in protopine is at 1658 cm.$^{-1}$ it appears that the "nitrogen bonding" can more than annul the shift towards higher wave numbers which would be caused by the loss of conjugation due to noncoplanarity of the carbonyl group and benzene ring.

EXPERIMENTAL

Protopine Hydriodide

The salt was obtained by adding potassium iodide to a solution of protopine in dilute hydrochloric acid. After recrystallization from water it was obtained as small colorless needles which gradually became discolored on heating, were black at 270°, but did not melt up to 300°. Calc. for $C_{20}H_{20}O_5NI$: C, 49.91; H, 4.19; one N–CH_3, 3.12%. Found: C, 50.11; H, 4.09; N–CH_3, 3.46%.

Protopine Methiodide

To protopine dissolved in chloroform was added a large excess of methyl iodide. After two days, colorless needles had separated which, after recrystallization from methanol, melted at 213–215° (dec.). Calc. for $C_{21}H_{22}O_5NI$: C, 50.93; H, 4.48; two N–CH_3, 6.07%. Found: C, 51.16; H, 4.60; N–CH_3, 5.07%.

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3. MOTTUS, E. H., SCHWARZ, H., and MARION, L. Can. J. Chem. 31: 1144. 1953.
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Contents

Page

The Photolysis of Acetone above 300° C.—*L. Mandelcorn and E. W. R. Steacie* - - - - - - - - - - - - - - - - - - 331

Preparation of 1-C^{14} Pentonic Acids by the Cyanhydrin Synthesis—*A. C. Neish* - - - - - - - - - - - - - - - - - - - 334

A Chemical Synthesis of D-Trehalose—*R. U. Lemieux and H. F. Bauer* - 340

Sulphur Isotope Effects in the Bisulphite Addition Reaction of Aldehydes and Ketones. II. Bond-formation Effect—*W. A. Sheppard, R. F. W. Bader, and A. N. Bourns* - - - - - - 345

The Reaction of Active Nitrogen with Propane—*M. Onyszchuk L. Breitman, and C. A. Winkler* - - - - - - - - - - - - 351

Addition Compounds of the Molecular Halides. III. The Trichlorides and Pentachlorides of Phosphorus, Arsenic, Antimony, and Bismuth with Triethylamine—*W. R. Trost* - - - - - 356

The Acetyl Group Migrations in D-Glucose Diethyl Thioacetyl Tetraacetate—*R. U. Lemieux and H. F. Bauer* - - - - - - 362

The Kinetics of the Pyrolysis of Ethyl and Isopropyl Formates and Acetates—*Arthur T. Blades* - - - - - - - - - - - - - 366

Studies in the Polyoxyphenol Series. VI. The Oxidation of Pyrogallol and Vanillin by Alkaline Hypoiodite and Hypochlorite—*G. Denis Thorn and C. B. Purves* - - - - - - - - - - 373

The Silver Catalyzed Oxidation of Ethylene. I. Slow Processes on the Catalyst Surface—*A. Orzechowski and K. E. MacCormack* - 388

Excited Molecules as the Reactive Species in Active Nitrogen—*R. A. Back, Margaret Menzies, and C. A. Winkler* - - - - - 399

Preparation of Some New Branched-chain Carbohydrates from D-α-Fructoheptonic Lactone—*R. J. Woods and A. C. Neish* - - 404

The Silver Catalyzed Oxidation of Ethylene. II. Kinetics of C_2H_4 Oxidation—*A. Orzechowski and K. E. MacCormack* - - - - 415

The Silver Catalyzed Oxidation of Ethylene. III. Kinetics of Ethylene Oxide Oxidation—*A. Orzechowski and K. E. MacCormack* - 432

The Silver Catalyzed Oxidation of Ethylene. IV. Reaction Mechanism—*A. Orzechowski and K. E. MacCormack* - - - - - - - 443

The Structure of Protopine Methiodide: A Correction—*F. A. L. Anet and Léo Marion* - - - - - - - - - - - - - - - - - - - 452

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